

# Inverse Spinel Pigments

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The system  $\text{Zn}_2\text{TiO}_4\text{-Co}_2\text{TiO}_4\text{-Ni}_2\text{TiO}_4$  yields a bright green pigment with the orthotitanate spinel structure. Brick-red, orange, and brown pigments are found in the system  $\text{Zn}_2\text{TiO}_4\text{-Co}_2\text{TiO}_4\text{-Fe}_2\text{TiO}_4$ .

## I. Introduction

THE development of inorganic pigment materials in general, and inverse spinel pigments in particular, is governed by a number of basic principles.

These principles of crystal chemistry may—as is appropriate for an empirical science—be summarized as a set of very general rules or guidelines which bring some order to rather extensive sets of empirical data.<sup>1</sup> These rules or guidelines enable the development of a rational correlation of the crystal structures of materials and the transformations between these structures and, hence, lead to knowledge of which chemical elements may appear in a given structure; or, taken the other way, which structures are available to contain given elements.

In the first place, the principal component of the free energy of an ionic solid material at room temperature is its lattice energy which, in turn, is determined almost totally by the nearest-neighbor cation-anion distances.<sup>1,2</sup> This concept derives from a consideration of the effects of bringing a collection of ions together into a lattice. At large distances, the ions attract or repel one another by Coulomb interaction of their charges. The potential function for this interaction is:

$$V = Z_a Z_c e^2 / R_{ac} \quad (1)$$

Here the  $Z$ s are the charges of the various ions and  $R_{ac}$  the distance between the ions. As the ions are brought closer together, so that their outer electron shells begin to overlap, an additional characteristic repulsive force becomes operative, resulting from the overlapping of the ions. It is this repulsive force that opposes the

Coulomb attractive force between a positive and a negative ion and causes them to come to equilibrium at a finite value of the internuclear distance. This characteristic repulsive potential falls off very rapidly in value with increase in  $R_{ac}$ . Therefore, we may write for the lattice energy:

$$U = \frac{N A e^2 Z_a Z_c}{r_a + r_c} \left( 1 - \frac{1}{n} \right) \quad (2)$$

Here  $r_a + r_c$  expresses the interionic distance as the sum of the sizes of the ions involved. The equation, in effect, reduces to the form:

$$U = K / (r_a + r_c) \quad (3)$$

Hence, the existence or stability of an ionic pigment is directly dependent on the charge of the ions and the interionic separation.

In the second place, the coordination polyhedra of the anions about each cation in ionic solid phases are determined almost unequivocally by the radius ratio.<sup>1,3</sup> In crystals containing highly charged cations, the most important terms in the expression for the crystal energy are those representing the interaction of each cation with the adjacent anions. The negative Coulomb energy of the cation-anion interactions causes each cation to attract a number of anions, which approach to the equilibrium distance from it.

If too many anions are grouped around one cation, the anion-anion repulsion becomes strong enough to prevent the anions from approaching closely to the cation. The decrease in Coulomb energy resulting from increase in the cation-anion distance then makes the structure less stable than another structure with fewer anions about each cation.

We may therefore calculate the minimum radius ratio for the stability of various coordination polyhedra.<sup>3</sup> For triangular coordination, the minimum radius ratio is 0.155; for tetrahedral coordination it is 0.225; for octahedral coordination 0.414; for cubic coordination 0.732; and for cubooctahedral coordination 1.000.

This illustrates the important conclusion that, for ionic compounds, the role of ionic radius and radius ratio dominates all other

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Table I. Values of the Ligancy for Cations with Oxygen Ion\*

Ion	Radius ratio	Predicted ligancy	Observed ligancy <sup>†</sup>	Strength of bond
$\text{B}^{3+}$	0.20	3 or 4	<u>3,4</u>	1 or 3/4
$\text{Be}^{2+}$	.25	4	<u>4</u>	1/2
$\text{Li}^{\dagger}$	.34	4	<u>4</u>	1/4
$\text{Si}^{4+}$	.37	4	<u>4,6</u>	1
$\text{Al}^{3+}$	.41	4 or 6	<u>4,5,6</u>	3/4 or 1/2
$\text{Ge}^{4+}$	.43	4 or 6	<u>4,6</u>	1 or 1/2
$\text{Mg}^{2+}$	.47	6	<u>6</u>	1/3
$\text{Na}^+$	.54	6	<u>6,8</u>	1/6
$\text{Ti}^{4+}$	.55	6	<u>6</u>	2/3
$\text{Sc}^{3+}$	.60	6	<u>6</u>	1/2
$\text{Zr}^{4+}$	.62	6 or 8	<u>6,8</u>	2/3 or 1/2
$\text{Ca}^{2+}$	.67	8	<u>7,8,9</u>	1/4
$\text{Ce}^{4+}$	.72	8	<u>8</u>	1/2
$\text{K}^+$	.75	9	6,7,8,9,10,12	1/9
$\text{Cs}^+$	.96	12	<u>12</u>	1/12

\*From Ref. 3. <sup>†</sup>Values underlined are those usually found for cation.

Table II. Effective Ionic Radii for the Major Pigmenting Ions\*

Ion	Radius for coordination number (nm)		
	IV	VI	VIII
$\text{Al}^{+3}$	0.053	0.067	
$\text{Co}^{+2}$	.071	.0885	
$\text{Cr}^{+3}$		.0755	
$\text{Cu}^{+2}$	.076	.087	
$\text{Fe}^{+2}$	.077	.092	
$\text{Fe}^{+3}$	.063	.0785	
$\text{Mg}^{+2}$	.072	.086	0.103
$\text{Mn}^{+2}$		.097	.107
$\text{Mn}^{+3}$		.0785	
$\text{Mn}^{+4}$		.068	
$\text{Ni}^{+2}$		.083	
$\text{Pb}^{+2}$		.132	.145
$\text{Pr}^{+3}$		.1137	.128
$\text{Pr}^{+4}$		.092	.110
$\text{Sb}^{+5}$		.075	
$\text{Sn}^{+4}$		.083	
$\text{Ti}^{+4}$		.0745	
$\text{V}^{+4}$		.073	
$\text{V}^{+5}$	.0495	.068	
$\text{Zn}^{+2}$	.074	.089	.104
$\text{Zr}^{+4}$		.086	.098

\*From Ref. 2.

considerations of structure, stability, and transformation. These figures, which are based on a hard-sphere model, predict that the 3-, 4-, 6-, 8-, or 12-sided polyhedra would be formed in the radius ratio ranged 0.155 to 0.225, 0.225 to 0.414, 0.414 to 0.732, 0.732 to 1.000, and  $>1.000$ .<sup>1</sup> The empirical fact is that there is a distribution of radius ratio for each coordination concentrated within these limits but extending beyond them. From the data on known structures, one can plot the frequency with which an ion of given size may be found in any of the two (or three) most probable coordinations. Such data are of great functional use to the molecular engineer in deciding what polyhedral cage a particular cation will demand. Thus, an ion in the range 0.35 to 0.4 Å (0.035 to 0.04 nm) is virtually certain to be in 4-fold coordinations, whereas those near 1.15 Å (0.115 nm) range from 12 to 6 coordination. Of course, other parameters such as crystal field stabilization energies from *d* or *f* electrons will affect these values, but the concept helps one to select plausible structures which can contain particular sets or cations.

Moreover, these rules do work quite well to predict the coordination of various cations.<sup>2</sup> Table I gives values for cation coordination to the oxygen ion. The observed ligancies given in the fourth column are seen to lie close to the predicted values. The underlined values are those usually found for the cation. The other values are observed in only a few crystals. In the cases where the observed ligancy deviates greatly from the expected value, such as 12 for potassium ions in crystals such as mica, it is probable that the other ions present play the most important part in determining the configuration. For example, tetrahedral coordination has been observed about  $\text{Si}^{4+}$  in scores of crystals, and octahedral coordination in only one,  $\text{SiP}_2\text{O}_7$  (which does not occur in nature); it is clear that this crystal is to be considered as exceptional.

The ions with transition values of the radius ratio are especially interesting. The aluminum ion forms oxygen tetrahedra in many aluminosilicates and octahedra in others; it has ligancies 4 and 6 in sillimanite, 5 and 6 in andalusite, and 6 alone in kyanite, all three stable minerals having the same composition  $\text{Al}_2\text{SiO}_5$ . Zirconium is octahedrally coordinated in several crystals, but has an irregular 8 coordination in zircon.

The third principle is that the structures which can be built from any combination of cations and anions are subject to the rules for electrostatic neutrality.<sup>3</sup> This principle can be illustrated by a consideration of silica ( $\text{SiO}_2$ ). In this material each silicon ion is surrounded by four oxygen ions at tetrahedron corners. In order for the stoichiometric ratio of one silicon ion to two oxygen ions to be retained it is accordingly necessary that, on the average, each oxygen ion act as a corner of two tetrahedra. This might be achieved by having alternate oxygen ions serve as corners of one tetrahedron and three tetrahedra, or in other such ways. The electrostatic valence rule requires, however, that each oxygen ion serve

as a corner of two tetrahedra. In other words, in a stable ionic structure the valence of each anion, with changed sign, is exactly or nearly equal to the sum of the strengths of the electrostatic bonds to it from the adjacent cations. Thus, referring now to the last column in Table I,  $\text{Si}^{4+}$  with a bond strength of 1 and a valence of 4 will be tetrahedrally coordinate. In the same material, oxygen with a valence of 2 will be bonded to 2 cations.

The fourth principle is that the coordination of a cation increases as the charge of the anion decreases, and decreases as the field strength increases.<sup>1</sup> For example, in some materials the coordination of the fluoride will be higher than that of the oxide.

These four principles lead to the conclusion that, given the composition of a single phase and its structural formula, inspection of a plot of the ionic radius of one cation versus that of a second cation in the structure, which is called a structure field map, permits determination of the probable structure(s) of the phase.<sup>1,2</sup> Knowing the ionic size of the ions of interest for pigmentation, one can then predict the phases which might be useful for development of pigment systems.

The ions which are of interest for pigmentation are those which are themselves colored.<sup>4,5</sup> Ionic coloration is the result of partially filled *d* or *f* shells, permitting transitions between the levels within those shells, with the absorption of energy at the optical frequencies. Therefore, the most common coloring ions are those of the first transition series V, Cr, Mn, Fe, Co, Ni, and Cu. In addition, the rare earths Ce, Pr, and Nd are occasionally used.

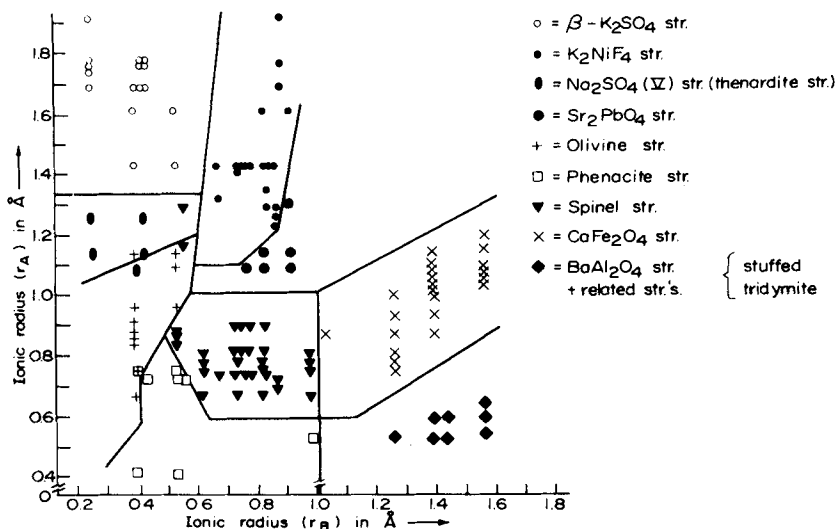
Several of these ions have more than one readily available valence state. Vanadium can be tetravalent or pentavalent; manganese divalent, trivalent, or tetravalent; iron divalent or trivalent; praseodymium trivalent or tetravalent.

In Table II are tabulated the effective ionic radii for the major pigmenting ions when they appear in tetrahedral, octahedral, or 8-fold coordination.<sup>2</sup> Those nonpigmenting ions such as aluminum, titanium, and zinc, which are commonly used for dilution, are also included. The most striking conclusion from this table is that practically all of the pigmenting ions have radii between 0.7 and 1.0, in particular between 0.75 and 0.95. One may, therefore, conclude that crystal structures which accommodate ions in the range 0.7 to 1.0 would be most likely to occur in pigment systems.

Figure 1 is a structure field map for systems having the  $\text{A}_2\text{BO}_4$  stoichiometry. Examining the region of interest reveals many compounds having the spinel structure. It is, therefore, not surprising that this system is the most common structure found in pigment systems.

The model material, from which the name spinel derives, is the mineral spinel,  $\text{MgAl}_2\text{O}_4$ .<sup>2,6,7</sup> This mineral is cubic in structure with  $a_0 = 8.083$  Å. In this structure, perfect  $\text{MgO}_4$  tetrahedra share corners with slightly distorted  $\text{AlO}_6$  octahedra. The octahedra are linked together in three dimensions with adjacent octahedra by

Fig. 1. Structure field map for  $\text{A}_2\text{BO}_4$  compounds (from Ref. 2, p. 76; used by permission).



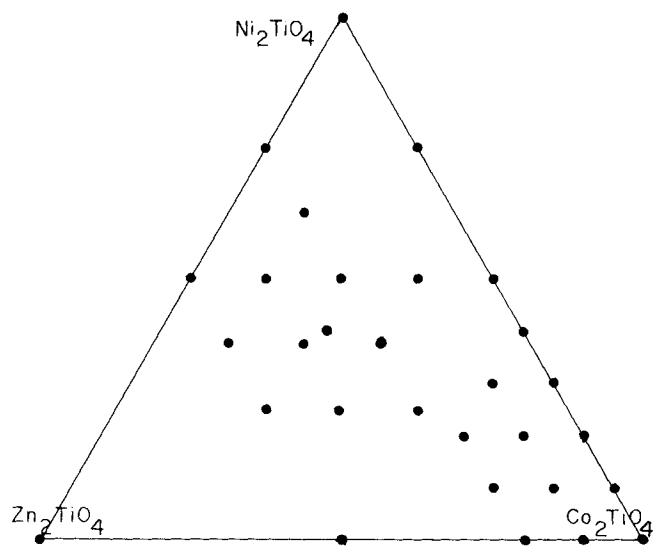


Fig. 2. Compositions studied in system  $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Ni}_2\text{TiO}_4$ .

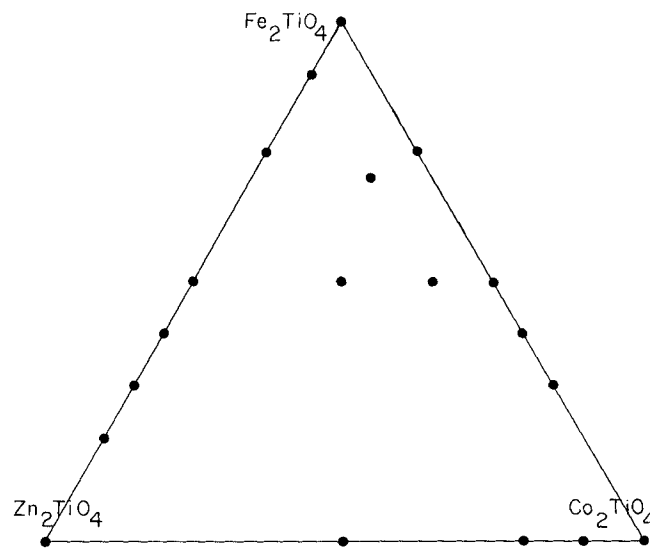


Fig. 3. Compositions studied in system  $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Fe}_2\text{TiO}_4$ .

sharing edges and with adjacent tetrahedra by sharing corners.

The structure can also be thought of as being made up of cubic close-packed layers of anions. The unit cell contains 32 anions and thus forms 64 tetrahedral interstices, of which 8 are occupied by cations and 32 octahedral interstices, 16 of which are occupied by cations. The distribution of metal ions in the structure is such that each oxygen atom is surrounded by four metal atoms (three aluminum and one magnesium) in the form of a slightly distorted tetrahedron. It must also be pointed out that the oxygen atoms do not form a perfect face-centered-cubic sublattice. Depending on the size of the included metal atoms, the oxygen atoms are displaced either toward the tetrahedral sites or in the reverse direction. As with all structures, there are definite ionic size relations among the constituent atoms which must be fulfilled. Because these relations are satisfied especially by the transition metals of the first period, the spinel structure is the most common of all the  $\text{A}_2\text{BX}_4$  structures.<sup>2,6</sup> Moreover, there are several varieties of spinels that can be synthesized. These include 1-6, 2-4, 3-2, 3-1, and 3-0 charge combinations.

Of all the different oxide spinels, the 3-2 are probably the most common and the most important with respect to pigment systems. In this system, the divalent ions can be magnesium, manganese, cobalt, nickel, copper, iron, and zinc. The trivalent ions can be aluminum, chromium, iron, and, less frequently, manganese, cobalt, and vanadium. Moreover, the spinels form an extensive series of mixed crystals among these various ions so that the compositional possibilities are practically limitless.

The pigments which are of this system<sup>8</sup> include blacks, the cobalt aluminate blues, the cobalt-zinc-alumina-chromium blue-greens, the chrome-iron-zinc and chrome-alumina-iron-zinc browns, and the majority of the chrome-alumina pinks.

The 2-4 spinels are also quite common and a few of them have recently been developed as pigments. These materials will now be considered in greater detail for their structure and their usefulness as pigments. In these materials the divalent ions can be magnesium, manganese, cobalt, nickel, copper, iron, or zinc. The tetravalent ions can be tin or titania.

When one considers spinels such as nickel ferrite or zinc titanate, one is surprised to find that the overall formula would suggest bivalent nickel occupying a tetrahedral site, whereas trivalent iron is known to prefer such an environment.<sup>6</sup> Alternatively, it is just as surprising should one find zinc in an octahedral site while titanium dioxide was found in a tetrahedral site. A more exact study has shown that these overall formulas cannot be used to derive the actual position of atoms in the crystal structure. Instead, the atoms in the formulation try to fit into those places most suitable for them. Thus, in nickel ferrite one iron ion goes into the

tetrahedral position and the nickel and the other iron ion occupy the two octahedral positions.

In zinc titanate, one zinc ion goes into the tetrahedral position, whereas the titania and the other zinc ion occupy the two octahedral positions. Materials such as this are called inverse spinels.

The properties of selected compositions among the inverse 2-4 spinels have been reported. They include brown  $\text{Mn}_2\text{TiO}_4$ ,<sup>9-11</sup> dark green  $\text{Co}_2\text{TiO}_4$ ,<sup>10-15</sup> brown  $\text{Fe}_2\text{TiO}_4$ ,<sup>11,16-20</sup> and white  $\text{Zn}_2\text{TiO}_4$ .<sup>10-12,14,20-25</sup> The compound  $\text{Ni}_2\text{TiO}_4$  cannot be made, but substantial nickel can be substituted into the ternary systems. The extent of nickel substitution for zinc in the system  $\text{Zn}_2\text{TiO}_4$ - $\text{Ni}_2\text{TiO}_4$  has been determined.<sup>26,27</sup> Complete solid solubility in the system  $\text{Co}_2\text{TiO}_4$ - $\text{Zn}_2\text{TiO}_4$  has been shown.<sup>27</sup> In the experimental work which follows, two ternary systems will be considered in some detail.

## II. Compositions

Compositions in the ternary system  $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Ni}_2\text{TiO}_4$  were prepared (Fig. 2). The ternary system  $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Fe}_2\text{TiO}_4$  was also studied (Fig. 3). These systems were chosen because a variety of colors can be obtained in them. The system  $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Ni}_2\text{TiO}_4$  yields various shades of green and yellow-green. The system  $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Fe}_2\text{TiO}_4$  yields brick-reds, oranges, and browns.

## III. Experimental Procedures

### (1) Sample Preparation

Technical-grade nickel carbonate, black iron oxide, zinc oxide, and cobalt oxide were used in these studies. The ingredients were weighted, blended, and micropulverized prior to use. Approximately 100 g samples were placed in 30 mL fireclay crucibles and covered for each firing.

The covered crucibles were calcined in a gas-fired kiln at 1080° to 1260°C, with a 3-h soak time. After cooling, the samples were removed from the crucibles and wet-milled to a mean particle size of 3 to 5  $\mu\text{m}$ .\*

### (2) Evaluation Procedure

The structure of the pigment was determined by X-ray diffraction (XRD) using conventional powder techniques on a diffractometer† with a Cu target operating at 50 kV and 25 mA. The scanning rate was 4°/min.

\*As measured on the Leeds and Northrup Microtrak particle size analyzer.

†XRD-5, General Electric Co., Schenectady, NY.

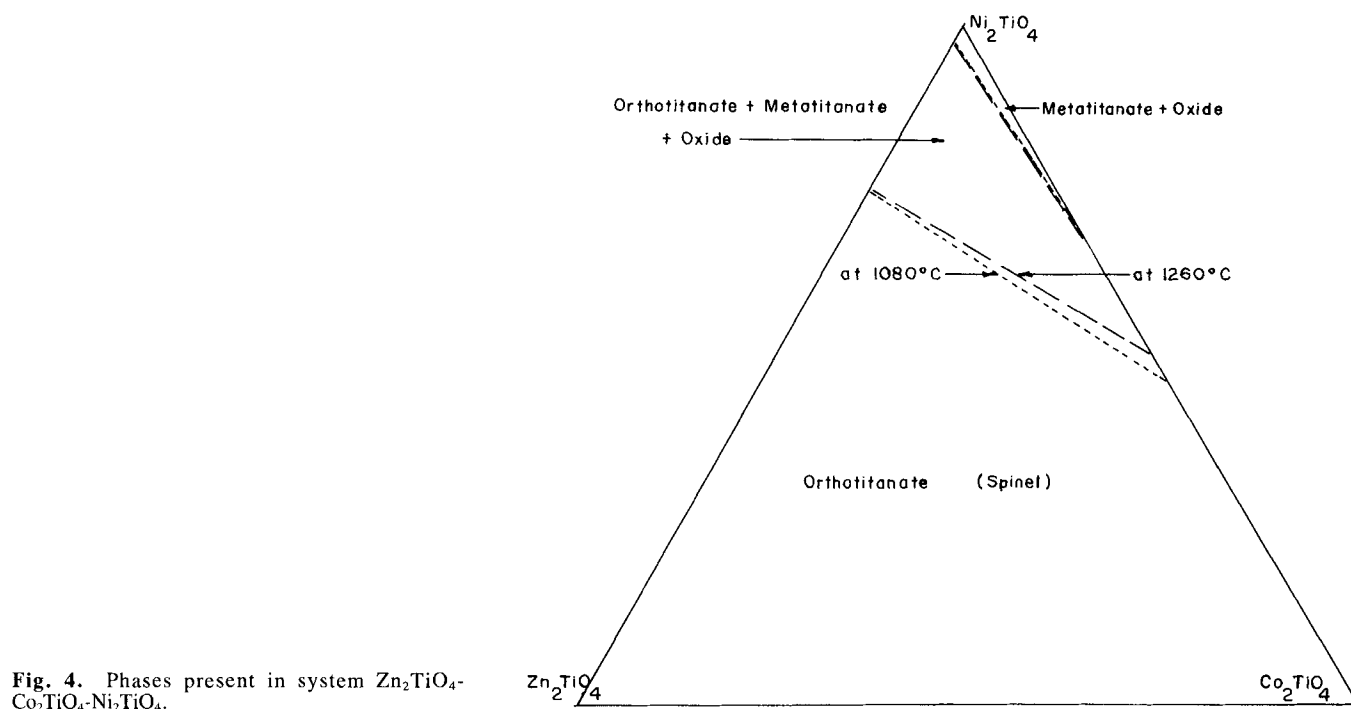


Fig. 4. Phases present in system  $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Ni}_2\text{TiO}_4$ .

To determine the lattice parameter of selected samples, the diffractometer was run at a scanning rate of  $0.4^\circ/\text{min}$  in the areas of the absorption bands. For this work, 20% of NaCl was added as an internal standard. The lattice parameter was determined with a computer program obtained from Argonne National Laboratory.<sup>28</sup>

To evaluate the color, the pigments were added to a paint of the following formulation (in grams): pigment 10.0, Soya oil alkyd resin 14.0, mineral spirits 16.5, naphtha 2.4, and driers 0.13.

After shaking for 30 min with 30 g of beads, the paint was strained and  $0.3 \text{ cm}^3$  of additional driers were added. The paint was drawn down on a 0.15 mm (0.006 in.) Bird applicator and allowed to air-dry for at least 24 h.

The color properties were measured on a visible spectrophotometer.<sup>†</sup>

#### IV. Results and Discussion

##### (1) The System $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Ni}_2\text{TiO}_4$

The XRD results for the nickel-containing ternary system are illustrated in Fig. 4. The orthotitanate spinel phase is stable over most of this field.

However, as has been reported,<sup>26,27</sup> the compound  $\text{Ni}_2\text{TiO}_4$  is unknown. Instead, a mixture of the metatitanate ( $\text{NiTiO}_3$ ) and unreacted NiO is found at all temperatures.

Although the compound  $\text{Ni}_2\text{TiO}_4$  is unknown, substantial amounts of NiO can be incorporated into the spinel structure. At  $1260^\circ\text{C}$  the phase boundary extends from 76% NiO along the join  $\text{Ni}_2\text{TiO}_4$ - $\text{Zn}_2\text{TiO}_4$  to 51% NiO along the join  $\text{Ni}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ . At  $1080^\circ\text{C}$  the boundary varies from 75% to 48%, respectively. The values for the  $\text{Ni}_2\text{TiO}_4$ - $\text{Zn}_2\text{TiO}_4$  join agree with those of Datta and Roy<sup>26</sup> at  $1260^\circ\text{C}$ . At  $1080^\circ\text{C}$ , the data reported here show more extensive spinel solubility.

This phenomenon has been ascribed to octahedral site preference by the nickel ions present.<sup>26</sup> Below 50% NiO, there is no need for NiO to assume a tetrahedral site, but above 50% NiO, there is. Thus, in the system  $\text{Ni}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ , the orthotitanate is stable only to approximately 50% NiO. In the system  $\text{Ni}_2\text{TiO}_4$ - $\text{Zn}_2\text{TiO}_4$ , some accommodation of NiO on tetrahedral sites is evidently possible, since up to 75% NiO is found in the orthotitanate phase.

Figure 5 shows the variation of the spinel lattice parameter along the joins  $\text{ZnNiTiO}_4$ - $\text{ZnCoTiO}_4$  and  $\text{ZnNiTiO}_4$ - $\text{CoNiTiO}_4$ . Along

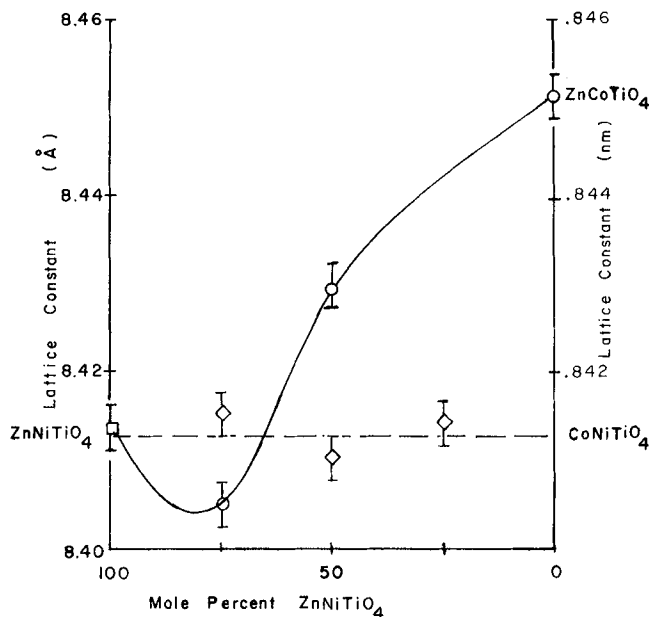


Fig. 5. Lattice constant variation for (—) system  $\text{ZnNiTiO}_4$ - $\text{ZnCoTiO}_4$  and (----) system  $\text{ZnNiTiO}_4$ - $\text{CoNiTiO}_4$ .

the latter join, there is no significant change in the lattice parameter as Co is substituted for Zn. On the other hand, the substitution of Co for Ni results in a very nonideal system. Up to 20% substitution lowers the lattice constant. Further increase raises the lattice constant.

This result can be understood by consideration of the relevant ionic radii. In the system  $\text{ZnNiTiO}_4$ - $\text{CoNiTiO}_4$  the zinc and cobalt ions will be primarily on tetrahedral sites, where  $r=0.71 \text{ Å}$  (0.071 nm) for Co and  $r=0.74 \text{ Å}$  (0.074 nm) for Zn. Any ions on octahedral sites have an even closer fit ( $r=0.885 \text{ Å}$  (0.0885 nm) for Co;  $r=0.90 \text{ Å}$  (0.090 nm) for Zn).

In contrast, for the system  $\text{ZnNiTiO}_4$ - $\text{ZnCoTiO}_4$ , a smaller

<sup>†</sup>Diano Corp., Woburn, MA.

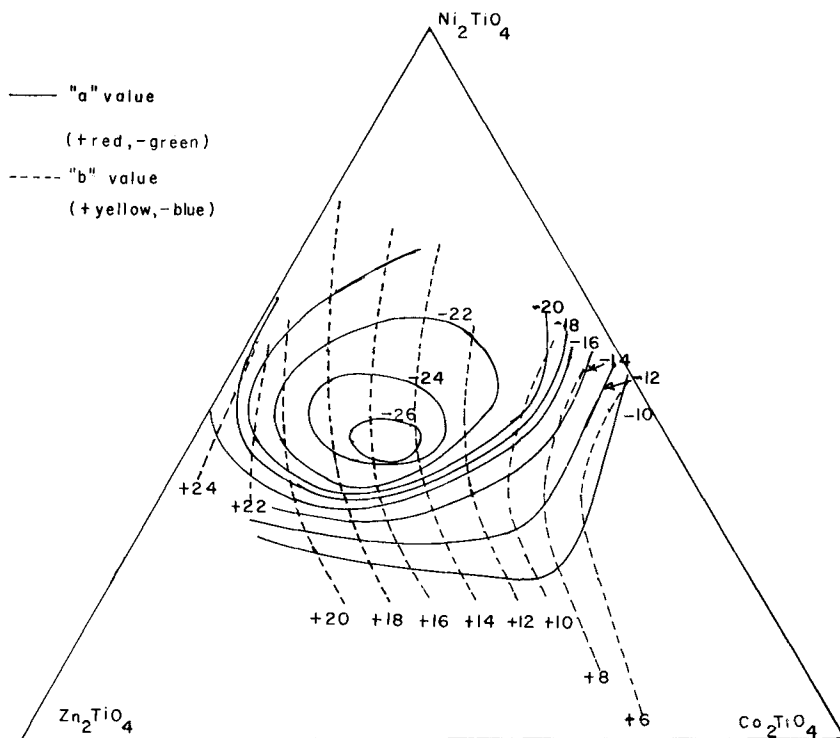


Fig. 6. Colors of pigments in system  $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Ni}_2\text{TiO}_4$  dispersed in an organic coating medium.

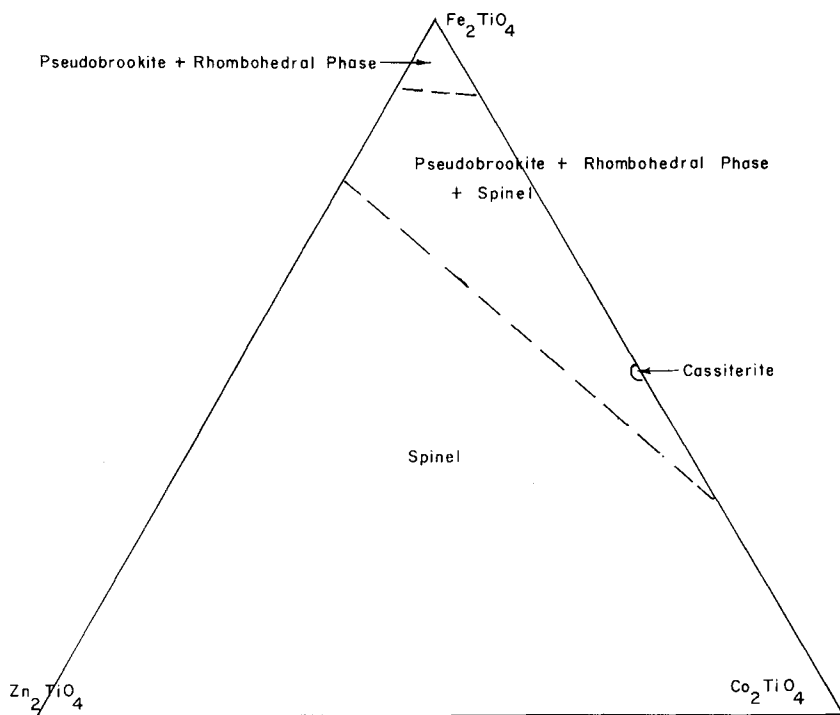


Fig. 7. Phases present in system  $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Fe}_2\text{TiO}_4$ .

nickel ion ( $r=0.83 \text{ \AA}$ ) (0.083 nm) is replaced by a larger cobalt ion ( $r=0.885 \text{ \AA}$ ) (0.0885 nm) on the octahedral sites. Moreover, there may be some randomization of site occupation, since cobalt does not have the strong octahedral site preference that nickel has.

Figure 6 shows the color coordinates obtained on the paint draw-downs made using the pigments in the  $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Ni}_2\text{TiO}_4$  ternary. The  $R_D$ ,  $a$ ,  $b$  system of color specification<sup>29</sup> is used here. In this system a red has a positive  $a$  value; a green a negative  $a$  value. A yellow has a positive  $b$  value; a blue a negative  $b$  value. The  $R_D$  value expresses lightness, from 0 for a dead black to 100 for a perfect white.

For clarity, the  $R_D$  values have not been included on this figure. The lines of constant lightness are approximately parallel to the lines of constant cobalt content. The yellowness increases in a regular manner as one proceeds across this figure. The lines of constant yellowness are approximately orthogonal to lines of constant nickel content.

The greenness values increase to a sharp peak in the middle of this figure at approximately 40% NiO, 25% CoO, 35% ZnO in the titanate spinel formulation. This intense color is the property desired in a commercial pigment. Hence this formulation is the basis for such a material.

## (2) The System $\text{Zn}_2\text{TiO}_4\text{-Co}_2\text{TiO}_4\text{-Fe}_2\text{TiO}_4$

The XRD results for the iron-containing ternary system are illustrated in Fig. 7. In this system also, the orthotitanate spinel is stable over most of the composition range.

The exception to stability of the spinel phase is at high iron concentration. Near the nominal  $\text{Fe}_2\text{TiO}_4$  composition, pseudobrookite and a rhombohedral phase are stable.

This behavior is understood in terms of the variable valence of iron in the system  $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ .<sup>18</sup> All three of these phases can accommodate the full range from divalent to trivalent iron. Spinel can vary from orthotitanate ( $\text{Fe}_2\text{TiO}_4$ ) to magnetite ( $\text{Fe}_3\text{O}_4$ ). The rhombohedral phase can vary from ilmenite ( $\text{FeTiO}_3$ ) to hematite ( $\text{Fe}_2\text{O}_3$ ), and pseudobrookite can vary from  $\text{FeTi}_2\text{O}_5$  to  $\text{Fe}_2\text{TiO}_5$ . At equilibrium in air, the composition  $\text{Fe}_2\text{TiO}_4$  is a mixture of pseudobrookite and the rhombohedral phase.<sup>18</sup> Zinc oxide does not have a trivalent state. Cobalt oxide is trivalent only under extreme conditions. Hence, additions of these materials shift the phase stability to the spinel phase.

The composition  $\text{FeCoTiO}_4$  yielded a unique phase of cassiterite structure. This result was reproduced at this composition, but was not obtained for any other formulation. The reason for this unique behavior is not known.

The variation of the spinel lattice constant along the join  $\text{FeZnTiO}_4\text{-CoZnTiO}_4$  from  $\text{FeZnTiO}_4$  to the extent of the spinel phase is shown on Fig. 8. There is a slight lowering of the lattice constant as cobalt is substituted for zinc.

The colors found along the  $\text{Fe}_2\text{TiO}_4\text{-ZnTiO}_4$  join are illustrated in Fig. 9. The scale for the  $a$  and  $b$  values is on the left side of the figure; that for the reflectance is on the right side. On the binary join the  $a$  values are all positive (red). The  $b$  values are also positive (yellow).

As the composition is varied from  $\text{Fe}_2\text{TiO}_4$  to  $\text{ZnTiO}_4$ , the reflectance and the yellowness ( $b$  value) increase. The redness increases up to the formula  $\text{FeZnTiO}_4$ , then decreases. Hence the color shifts from a brick-red for  $\text{Fe}_2\text{TiO}_4$  through dark oranges to a bright orange for  $\text{FeZnTiO}_4$ . As more zinc is added the color becomes a lighter and yellower orange.

Additions of even small quantities of cobalt to this system lead to very dark green, brown, and black, as shown on Fig. 10. Compositions near  $\text{Co}_2\text{TiO}_4$  are very dark green. Over most of the rest of the field one finds dark browns up to approximately 40%  $\text{Zn}_2\text{TiO}_4$ .

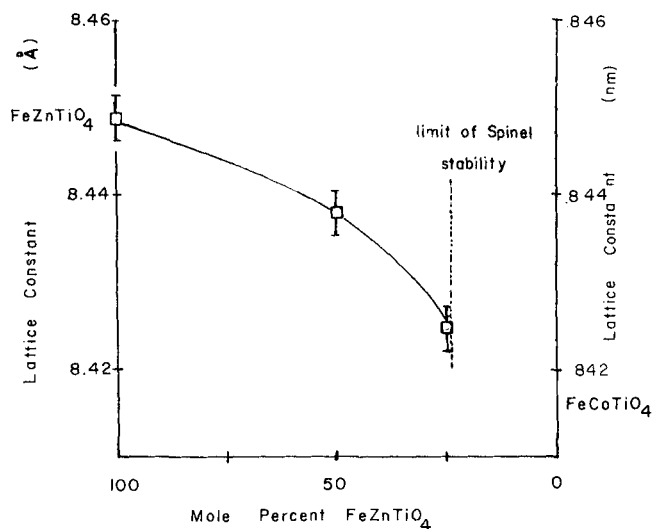


Fig. 8. Lattice constant variation in system  $\text{FeZnTiO}_4\text{-FeCoTiO}_4$ .

The unique cassiterite composition  $\text{CoFeTiO}_4$  also has a unique brick-red color.

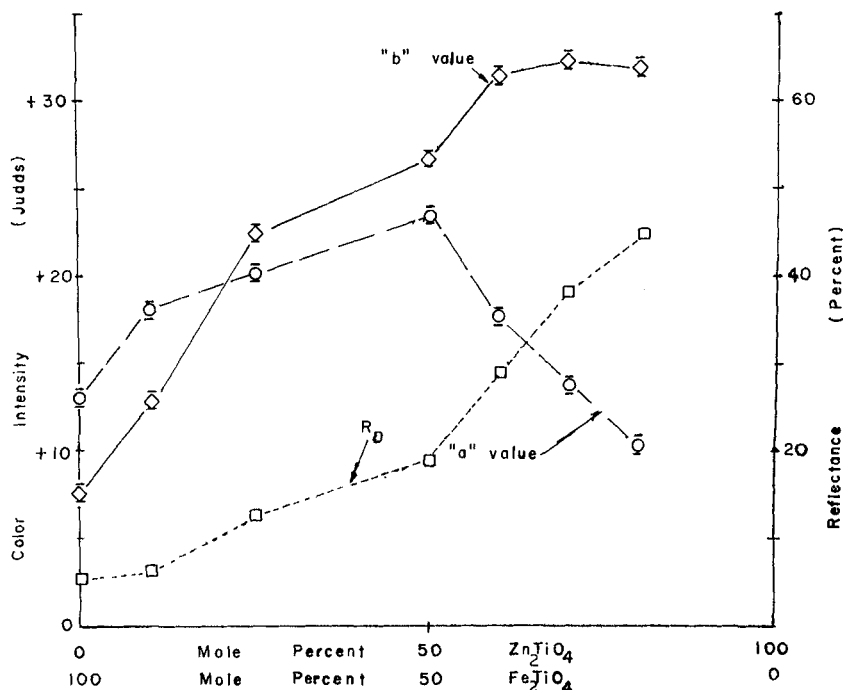
Thus this single ternary system offers a variety of pigment possibilities. These include brick-reds, bright oranges, and dark browns. It is rare for a single system to be so variable.

## V. Conclusions

In the system  $\text{Zn}_2\text{TiO}_4\text{-Co}_2\text{TiO}_4\text{-Ni}_2\text{TiO}_4$ , the orthotitanate spinel phase is stable over most of the compositional field. The exception to this conclusion is for compositions high in  $\text{Ni}_2\text{TiO}_4$ , which disproportionate to  $\text{NiTiO}_3$  and  $\text{NiO}$ . Substitution of cobalt for zinc in this system is ideal, whereas substitution of cobalt for nickel is highly nonideal.

In the system  $\text{Zn}_2\text{TiO}_4\text{-Co}_2\text{TiO}_4\text{-Fe}_2\text{TiO}_4$ , the orthotitanate spinel phase is also stable over most of the compositional field. The exception to this conclusion is for compositions high in iron. In the latter case, the variable valence of iron leads to regions of stability

Fig. 9. Colors of pigments in system  $\text{Zn}_2\text{TiO}_4\text{-Fe}_2\text{TiO}_4$  dispersed in an organic coating medium.



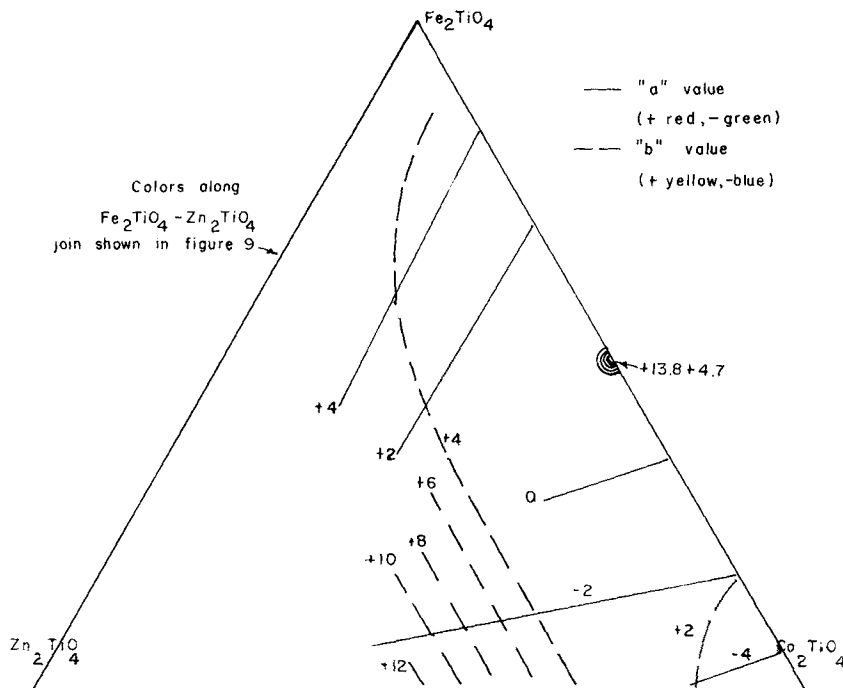


Fig. 10. Colors of pigments in system  $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Fe}_2\text{TiO}_4$  dispersed in an organic medium.

for pseudobrookite and a rhombohedral phase, the end-members of which are ilmenite and hematite. A unique cassiterite phase is found for the composition  $\text{FeCoTiO}_4$ .

A strong green coloration is found in the spinel portion of the system  $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Ni}_2\text{TiO}_4$ , at approximately 40%  $\text{TiO}_2$ , 25%  $\text{CoO}$ , 35%  $\text{ZnO}$  in the titanate spinel formulation.

On the binary join  $\text{Zn}_2\text{TiO}_4$ - $\text{Fe}_2\text{TiO}_4$ , a bright orange is found for orthotitanate spinel formulations near the composition  $\text{FeZnTiO}_4$ . In the pseudobrookite + rhombohedral phase region near  $\text{Fe}_2\text{TiO}_4$ , brick-red colors are found. In the ternary  $\text{Zn}_2\text{TiO}_4$ - $\text{Co}_2\text{TiO}_4$ - $\text{Fe}_2\text{TiO}_4$ , very dark green, brown, and black are found.

## VI. The Future of Pigment Research

The inverse spinels which have just been discussed are an example of what can be done to expand knowledge of pigment-forming systems and to find useful new pigments for various applications in glazes, porcelain enamels, paints, and plastics.

There is a continuing need for new systems in response to changes in the economic environment. Costs of various raw materials change, sometimes drastically. The Toxic Substances Control Act, and other environmental legislation, are eliminating some of the materials currently used. While on the one hand these are problems, on the other hand they are opportunities.

One example of the opportunities created by environmental regulation is the pigments discussed in this paper, which are a portion of the effort to replace chromium-bearing pigments. Hexavalent chromium, which is present in pigments such as  $\text{PbCrO}_4$  and  $\text{SrCrO}_4$ , is known to be a carcinogen.<sup>30</sup> Even trivalent chromium, while much less toxic, is suspect.

Hence a major trend at this time is to find suitable replacements for the many chromium-containing pigments. A possibility to replace chromium green is the pigments discussed in this paper. No completely satisfactory solution to the replacement of chromium yellows has been found. When color is the only requirement, nickel-doped rutile, together with organic pigments, can be used. When corrosion resistance is also required, no solution has been found.

An example of the response to cost escalation is the cobalt-free black pigments developed recently.<sup>31,32</sup> A few years ago a shortage in cobalt arose in response to political problems in Africa. This resulted in a sharp rise in the price of cobalt-bearing materials. It

was, therefore, possible to develop and introduce a nickel ferrochromite spinel pigment with a significant economic advantage.

Hence, there continue to be opportunities for useful research into pigment systems, their structure, phases, and transformations.

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# Barium Titanate Perovskite Sintered with Lithium Fluoride

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The sintering of barium titanate with, respectively, 1 and 2 wt% LiF for two stoichiometries, Ti/Ba=1 and 0.975, was studied using two calcined powders. One was pure barium titanate; the other contained BaTiO<sub>3</sub> plus BaCO<sub>3</sub> and TiO<sub>2</sub> that did not react when burning. The sintering chronology—intermediate phases, appearance, and disappearance of a liquid phase that has been pointed out for the first time—is directly dependent on the used calcined powder, on the LiF amount, and on the firing schedule. In the same way, the obtained perovskite symmetry varies during sintering from tetragonal to cubic and then to a second tetragonal form, whereas most of the Li and F disappear from the ceramic with two different kinetics.

## I. Introduction

CERAMICS with rather high dielectric constants, i.e. with  $\epsilon \approx 5000$ , which can be sintered at  $T < 1000^\circ\text{C}$  are of interest for making cheaper multilayer ceramic capacitors. Among the materials available, barium titanate, BaTiO<sub>3</sub>, with LiF added as a sintering aid has been considered as a potential candidate. The possibility of sintering BaTiO<sub>3</sub> with LiF was first studied by Walker *et al.*<sup>1</sup> Amin *et al.*<sup>2</sup> and Anderson *et al.*<sup>3</sup> showed that it was possible to sinter barium titanate in the presence of LiF at  $T < 900^\circ\text{C}$ . However, very long soak times (as long as 265 h) at these temperatures were necessary to obtain dielectric constants close to 4000 and low dissipation factors. Haussonne<sup>4,5</sup> studied sintering in this system, but considered only short sintering times of the sort useful in industrial synthesis. The Ti/Ba ratio and the amount of lithium fluoride influenced both densification and dielectric properties. More recently, it was shown that the densification and the evolution of dielectric properties vs temperature were related to the presence of a new pseudocubic perovskite.<sup>6</sup> It was also observed that the nature of the starting materials and the mixing and grinding techniques drastically influence the densi-

fication and the characteristics of the ceramics.<sup>7</sup> The influence of various fluorides on densification of barium titanate was also studied by Beauger *et al.*<sup>8</sup> From the prior studies it appears that the best results are obtained for Ti/Ba ratios  $< 1$ . In this study an attempt was made to achieve an understanding of the sintering phenomenon. The present work deals with a systematic study of the compositions Ti/Ba=0.975 and 1, in order to establish correlations between the densification, the structure, the changes in lithium and fluorine content in the materials during sintering cycles, and the dielectric characteristics.

## II. Experimental Procedure

Two calcined materials were studied,<sup>7</sup> labeled A and B. The A products contained, in addition to tetragonal BaTiO<sub>3</sub>, some BaCO<sub>3</sub> and TiO<sub>2</sub> which had not reacted, and small amounts of nonidentified phase(s). In the B products only tetragonal BaTiO<sub>3</sub> was observed by X-ray diffraction (XRD). For every sample A and B, two compositions were studied corresponding to Ti/Ba=0.975 and Ti/Ba=1, labeled A<sub>1</sub>, A<sub>2</sub> and B<sub>1</sub>, B<sub>2</sub>, respectively. A<sub>1</sub> and A<sub>2</sub> were prepared by dry-mixing BaCO<sub>3</sub>\* and TiO<sub>2</sub>\* in a shaker mill and by calcining these mixtures at  $1150^\circ\text{C}$  for 1 h. B<sub>1</sub> and B<sub>2</sub> were prepared from BaCO<sub>3</sub>\* and TiO<sub>2</sub>\* mixed by wet-milling in alcohol for 1/2 h and then calcined at  $1150^\circ\text{C}$  for 1 h.

One percent in weight of technical LiF\* (BET specific area:  $3.1 \text{ m}^2\text{g}^{-1}$ ) was added to these prefired A compounds, whereas the B calcined products were divided into two parts to which 1% and 2%, respectively, of LiF were added. The mixtures were homogenized in a ball mill, using alcohol.

Thermogravimetric and thermogravimetric analysis were conducted using a microbalance<sup>†</sup> on pressed powders of the calcined products and also on the LiF-added products, using a  $300^\circ\text{C}\cdot\text{h}^{-1}$  heating rate.<sup>‡</sup>

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‡Some of the analyses were performed at the Caracterisation Physico-Chimique Laboratory, Dept. ICM/MPA, CNET, Lannion, France.

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