

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
28 February 2002 (28.02.2002)

PCT

(10) International Publication Number  
**WO 02/16263 A1**

- (51) International Patent Classification<sup>7</sup>: **C01B 25/36**, C01F 7/00
- (21) International Application Number: PCT/US01/41790
- (22) International Filing Date: 20 August 2001 (20.08.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 09/644,495 23 August 2000 (23.08.2000) US
- (71) Applicant (for all designated States except US): **APPLIED THIN FILMS, INC.** [US/US]; 1801 Maple Avenue, Suite 5316, Evanston, IL 60201 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **SAMBASIVAN, Sankar** [US/US]; 2210 W. Arthur Avenue #3, Chicago, IL 60645 (US). **STEINER, Kimberly, A.** [US/US]; 534 W. Brompton #3N, Chicago, IL 60657 (US).
- (74) Agents: **DEKRUUF, Rodney, D.** et al.; Reinhart, Boerner, Van Deuren, Norris & Reiselbach, S.C., Attn. Linda, Gabriel, 1000 North Water Street, Suite 2100, Milwaukee, WI 53202-3186 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/16263 A1

(54) Title: HIGH TEMPERATURE AMORPHOUS COMPOSITION BASED ON ALUMINUM PHOSPHATE

(57) Abstract: A composition providing thermal, corrosion, and oxidation protection at high temperatures is based on a synthetic aluminum phosphate, in which the molar content of aluminum is greater than phosphorus. The composition is annealed and is metastable at temperatures up to 1400 °C.

## HIGH TEMPERATURE AMORPHOUS COMPOSITION BASED ON ALUMINUM PHOSPHATE

### Background of the Invention

This invention relates to synthetic inorganic compositions which remain metastable and possess other desired properties at mid and high temperature, for example, from 800°C to 1400°C and greater.

It is known to use metal oxide coatings for high temperature protection of substrates or other surfaces. Up to the present time, however, there are no known synthetic oxides which can remain amorphous and metastable at temperatures up to 1400°C or greater. Silica, for example, is known to devitrify/crystallize at temperatures slightly greater than 850°C. Other non-oxide materials, such as silicon oxy-carbide and silicon oxy-nitride rapidly oxidize and form crystalline phases at high temperatures in air.

Aluminum phosphate is a well known inorganic material that has found many uses in applications including catalysts, refractories, composites, phosphate bonded ceramics, and many others. Aluminum phosphate has a low density ( $d = 2.56 \text{ g/cm}^3$ ). It is chemically inert and stable at high temperatures, as well as being chemically compatible with many metals and with most widely used ceramic materials including silicon carbide, alumina, and silica over a moderate range of temperatures.

Aluminum phosphate, however, is unsuitable for use as a high temperature ceramic material because it undergoes polymorphic transformations (quartz-type, tridymite and cristobalite) with corresponding large molar volume changes. Thus, it would be desirable to provide a synthetic form of aluminum phosphate which is metastable and remains substantially amorphous at increasing temperatures, or during heating and cooling cycles. Another desirable property would be to provide an aluminum phosphate composition having a low oxygen diffusivity at high temperatures or in harsh environments, in order to provide oxidation protection and corrosion resistance to substrates such as metals and ceramics.

### Summary of the Invention

The present invention relates generally to substantially amorphous aluminum phosphate materials and/or compositions exhibiting metastability and various other

related properties under high temperature conditions. In part, metastability can be evidenced by retention of amorphous characteristics under oxidizing conditions, such morphology and the extent thereof due at least in part to the aluminum content of such materials/compositions, with those having an overall stoichiometric excess of aluminum exhibiting enhanced amorphous character and associated stability as compared to their stoichiometric counterparts. Such properties and related high-temperature attributes can be effected in the preparation of such materials/compositions, primarily by admixture of the aluminum precursor to the corresponding phosphate precursor to initiate various structural and/or compositional modifications which manifest themselves in the high temperature performance of the resulting aluminum phosphate material/composition. In particular, and as illustrated more clearly in the following examples, aluminum can be identified upon addition to a phosphate precursor and shown as contributing to the amorphous character and associated metastability of the resulting aluminum phosphate material/composition. Addition of a stoichiometric excess of aluminum precursor enhances the resulting amorphous character and metastability.

In part, the present invention is a metastable material including an aluminum phosphate composition, such a composition as can be represented having the formula  $\text{Al}_1 + x \text{PO}_{4 + 3x/2}$  wherein x is about 0 to about 1.5. The composition of such materials can be characterized by structural/compositional components absorbing radiation in the infra red spectrum at about  $795 \text{ cm}^{-1}$  to about  $850 \text{ cm}^{-1}$ , and can be further characterized by their presence at temperatures of at least about  $1000^\circ\text{C}$ . Without regard to any particular material or compositional phase, in various preferred embodiments of this invention, as discussed more fully below, x is 0 or about 0. In various other preferred embodiments, depending upon desired performance properties of the metastable material and/or end use application, x is about 0.1 to about 1.0. Generally, such materials are substantially amorphous, the degree to which in part dependent upon the value of x and the aluminum content of the entire composition. Depending upon such content and morphology, such materials are metastable at temperatures at least about  $1200^\circ\text{C}$ . As illustrated below, in the following examples, such materials can also include crystalline particles including but not limited to  $\text{CaWO}_4$ ,  $\text{Al}_2\text{O}_3$  and  $\text{ErPO}_4$ , such inclusions as can result from temperature treatment and/or incorporation of suitable precursor components. Such inclusions can be provided, as desired, to affect various material physical characteristics and/or

performance properties, including, but not limited to, modification of the material thermal expansion coefficient for a particular end use or composite fabrication.

In light of the above and in conjunction with the following examples and detailed descriptions, the present invention can also be a method of using the aluminum content of an aluminum phosphate composition to affect and/or control the metastability thereof. Such a method includes providing an aluminum phosphate composition from or using an aluminum salt precursor compound. The resulting aluminum phosphate composition has an aluminum content corresponding to that of the precursor compound, such aluminum content sufficient to provide a desired and/or predetermined compositional metastability. As illustrated below, and as would be understood to those skilled in the art, metastability of such a material can be evidenced spectroscopically showing an amorphous and/or non-crystalline aspect of the material. The material can have a certain metastability with an aluminum content stoichiometric with respect to phosphate. Generally, the metastability of such a material can be enhanced with a stoichiometric excess of aluminum.

Aluminum content and resulting stability can be effected upon preparation of the corresponding precursor and admixture with a suitable phosphate precursor, as illustrated elsewhere herein. Metastability and various other optical, chemical and/or physical properties can benefit by inclusion of other metal components including but not limited to silicon, lanthanum and zirconium upon choice of and/or modification of a suitable precursor.

Accordingly, the present invention also includes, in part, a method for preparing a precursor solution for the formation of a metal phosphate composition, preferably an aluminum phosphate composition. Such a method includes preparation of a first solution of a metal and/or aluminum salt; preparing a phosphorus component; and admixing the solution and component. Typically, the phosphorus component is an alcoholic solution of phosphorus pentoxide, but other phosphorus components/phosphate precursors can be used with comparable effect as described elsewhere herein. Likewise and without limitation, the metal/aluminum component is provided in alcoholic solution, with choice of solvent dependent upon metal/aluminum solubility and compatibility with the corresponding phosphorus/phosphate component. Among the various departures from the prior art, this aspect of the present invention contemplates use of a stoichiometric excess of the corresponding metal and/or aluminum component in the preparation of such

a precursor and use thereof in the subsequent formation of the desired metal and/or aluminum phosphate material/composition. As described more fully elsewhere herein, preferred embodiments of this invention are directed toward suitable aluminum salt components, precursors and resulting materials/compositions, but various other metal components can be incorporated into the precursor solution to provide the resulting material/composition associated thermal, optical, chemical and/or physical properties.

In part, the present invention also includes a method of using an aluminum phosphate composition to enhance the oxidation resistance of an associated substrate. The method includes (1) providing an aluminum phosphate composition of this invention, preferably one having the formula  $\text{Al}_{1+x}\text{PO}_{4+3x/2}$ , wherein x is about 0 to about 1.5; and (2) applying the composition to a suitable substrate. In various preferred embodiments, depending upon end use application and/or fabrication technique, the composition can be annealed either prior or subsequent to substrate application. Regardless, as illustrated below, such a composition can be dip-coated to provide a film on the substrate.

Alternatively, without limitation, the composition can be prepared as a powder then either plasma—or aerosol—sprayed onto a substrate.

In part, the present invention can also include an aluminum phosphate product with aluminum-oxygen-aluminum structural moieties, absorbing radiation in the infra red spectrum at about  $795\text{ cm}^{-1}$  to about  $850\text{ cm}^{-1}$ . Such a product is obtainable and/or can be produced by (1) mixing an alcoholic solution of phosphorus pentoxide with a solution of an aluminum salt, the salt either stoichiometric or in stoichiometric excess with respect to the phosphorus precursor; and (2) heating the resulting admixture. Such a product is substantially amorphous, but can also provide for crystalline particulate inclusions, as discussed above. As a representative embodiment, such particles are crystalline erbium phosphate inclusions prepared by incorporating an erbium salt with the aforementioned aluminum salt solution. Alternatively, illustrating another aspect of this invention, the product can include Group III A and/or Group III B-VI B metal oxide particles in amounts sufficient to modify the thermal expansion coefficient of the resulting product.

With regard to one or more aspects of the preceding discussion, the present invention can include a new class of phosphate compounds formulated to contain an excess amount of metal species in the composition; that is, with reference to a preferred embodiment, the aluminum atoms exceed the number of phosphorus atoms found in

stoichiometric aluminum phosphate. The excess can be more than one percent and preferably greater than five percent.

Whether compositions of this invention are stoichiometric or reflect an excess metal component methods for their preparation include those disclosed in U.S. Patent No. 6,036,762, the entirety of which is incorporated herein by reference. In accordance therewith, a precursor solution is formed from two liquid components. The first component is a metal salt dissolved in alcohol. The second component of phosphorus pentoxide is dissolved in alcohol. The two components are then mixed together in the desired molar proportions to provide a stable precursor solution, with the phosphate portion at least partially esterfying to form a polymer-like structure which uniformly entraps the metal ion.

The solution, as such, may be heated directly to remove the alcohol portion and other species and provide a pure metal phosphate. Preferably, however, the solution is applied as a coating to a non-porous or porous substrate using any suitable method, and the coated substrate is heated, typically to a temperature of less than 600°C, to obtain a uniform and pure coating of the metal phosphate on the substrate.

A particular advantage of this approach is that the precursor solution provides a substrate coating of even and uniform thickness for substrate application. After initial heat treatment, subsequent coatings may be applied to increase coating thickness. This methodology is applicable to the formation of precursor phosphate solutions containing more than one metal ion. The ability to adjust the concentration of the composite solution over a wide range is another distinct advantage, allowing for precise or controlled amounts of metal phosphates to be formed.

Further and as directed more particularly to the present invention, the aforementioned admixture/precursor solution can be dried and then annealed, for example, at temperatures of up to 800°C or greater, in air. The annealing step is believed to cause a transformation of the molecular structure, with the final product being more than 50% amorphous in content, and with the amorphous nature being sustained for long periods at temperatures up to 1400°C or greater without oxidation. Depending on the synthetic procedure and presence of other components or additives, the composition may also contain small crystalline inclusions which can impact other desirable properties, such as toughness and optical activity. The composition exhibits other desirable properties,

such as very low oxygen diffusivity, low thermal conductivity and high emissivity. Thus, a particularly suitable application is to use the composition as a coating on a substrate to minimize oxidation of the substrate at high temperatures.

The initially formed organic solution can be converted into any desired form. For example, the solution may be applied to a metal, ceramic or other substrate, such as ceramic composites and then annealed, or it may be converted into any desired shape, such as fibers or filaments or in any other desired molded form, or may be converted into a powder for application to substrates using a suitable spray technique. Various other end use applications are provided elsewhere, herein. Various materials/composites of this invention are available under the Cerablak trademark from Applied Thin Films, Inc.

#### Brief Description of the Drawings

Fig. 1. Uncoated and AlPO<sub>4</sub> coated type 304 stainless steel after 1000°C 100 h. The coated piece showed remarkably little weight gain from oxidation (0.08-0.24%) compared to the uncoated piece (4.5-8.6%).

Fig. 2. TEM micrographs of powders annealed to a) 1200°C 420h b) 1300°C 100h c) 1400°C 10h d) electron diffraction 1200°C 100h.

Fig. 3. TEM micrograph of a coating on a Nextel 720 fiber, with an alumina overcoat, annealed 1200°C 2h.

Fig. 4. XRD pattern of a stoichiometric material annealed to a) 1100°C for 1 hour, b) 1100°C for 163 hours. Note the splitting of the peak at 21.5, indicating the presence of crystalline tridymite and cristobalite phases.

Fig. 5. a) XRD pattern of an aluminum phosphate material (x=0.75) annealed at 1100°C for 1 hour, b) XRD pattern of the same composition annealed to 1100°C for 163 hours. Note the lack of differentiation of the tridymite peaks.

Fig. 6. Thermal expansion measurements for an aluminum phosphate composition, in accordance with this invention.

Fig. 7. TEM micrograph and electron diffraction pattern of AlPO<sub>4</sub> coated Nextel 720 fiber annealed to 1200°C for 100 hours.

Fig. 8. TEM bright field image of AlPO<sub>4</sub> nanocrystal embedded in the amorphous matrix.

Fig. 9. TEM micrograph of Er-doped aluminum phosphate annealed to 1000°C for 1 hour.

Fig. 10. a) Thermal conductivity of AlPO<sub>4</sub> (lower line) with YSZ, fused silica, mullite alumina and spinel. b) Thermal conductivity of AlPO<sub>4</sub> (lower line) and YSZ, a common thermal barrier material.

Fig. 11. SEM micrograph of a cross-section of an AlPO<sub>4</sub> fiber.

Fig. 12. X-ray diffraction patterns of a) powder annealed at 1100°C, 1 hr and b) powder annealed at 1200°C, 500hr, 10 atm, 15% steam (white).

Fig. 13. TEM micrograph of crushed white pellet of Example 31, showing nanocrystalline inclusions in an amorphous matrix and electron diffraction pattern from different area of the same sample.

Fig. 14. Raman spectra from AlPO<sub>4</sub> annealed 1400°C, 1hr; a) black area, and b) white area from the same material/composition sample.

Fig. 15. <sup>31</sup>P NMR of phosphorus pentoxide dissolved in ethanol. a) soon after dissolution b) after 24 hours reflux.

Fig. 16. Liquid <sup>31</sup>P NMR spectra of admixed precursor solutions, showing the effect of aluminum addition. a) full spectrum b) plot showing peaks reflecting the presence of aluminum.

Fig 17. X-ray diffraction patterns of the solutions shown in Fig. 16 after anneal to 1100°C, 160 hrs. a) full scale b) zoom to show the differences in the peaks near 21°.

Fig. 18. FTIR of stoichiometric and non-stoichiometric compositions annealed to 1100°C for 1 hr.

Fig. 19. Deconvolution of <sup>27</sup>Al NMR spectrum of stoichiometric AlPO<sub>4</sub> annealed to 1100°C, 1hr.

Fig. 20. Deconvolution of <sup>27</sup>Al MAS NMR of an excess aluminum composition Al/P=2 (1-fold excess, x = 1.0) after anneal at 1100°C, 160h.

#### Detailed Description of Several Preferred Embodiments

As discussed above, the present invention relates to a new class of metastable high-temperature amorphous inorganic compositions. A unique amorphous structure can be derived using a simple, low-cost sol-gel precursor. The thermal stability of the amorphous material is primarily controlled by metal content of the corresponding precursor, aluminum in preferred embodiments. Several compositions have been

synthesized in amorphous form and shown to be stable for hundreds of hours above 1200°C. Most crystalline materials of the prior art synthesized using sol-gel routes undergo amorphous to crystalline transition below 1000°C. In this case, however, and with aluminum phosphate as a generic example, thermodynamic equilibration to stable crystalline alumina and AlPO<sub>4</sub> phases does not occur until annealing above 1500°C. Calorimetric measurements revealed highly exothermic dissolution behavior suggesting the material to be thermodynamically unstable or metastable. Extremely low oxygen diffusivity in the amorphous material, which may be attributed to a special "Al-O-P" cluster, appears to be dominating the sluggish kinetics. Hermetically dense and adherent thin films (1000 Å or less) deposited by a simple dip coating process demonstrate remarkable ability of the material to protect stainless steel from oxidation at 1000°C (see, Fig.1 and Example 2, below).

When prepared as a film or coating, the material tends to remain completely amorphous whereas powders derived therefrom contain amorphous material with minor amounts, up to about 20-30%, of nanocrystalline inclusions (varying in size from 5-60 nm) of stoichiometric aluminum phosphate (Figs. 2 and 3). Likewise, as described elsewhere herein, the amorphous content and presence of nanocrystalline inclusions can also be affected by the stoichiometry of an aluminum precursor, with the use of a stoichiometric excess thereof reducing the incidence of such inclusions, increasing amorphous content and enhancing the metastability of the entire material/composition. Several properties characterizing such compositions of this invention are provided in Table 1, below.

Table I. Selected Illustrative Properties

Oxygen Diffusivity	$\sim 1 \times 10^{-12}$ cm <sup>2</sup> /sec (chemical diffusivity @ 1400°C)
Thermal expansion	$5 \times 10^{-6}$ K <sup>-1</sup>
Thermal conductivity	1.0-1.5 W/mK (RT-1300°C)
Dielectric constant	3.3-6.35 (for x=0.5-0.75)

The very low oxygen diffusivity allows for the use of extremely thin amorphous protective coatings (50-100 nm) where cracking due to thermal stresses is less of a concern. This unique property can be exploited to provide protection for many metals and ceramics used in high temperature applications. Formation of nanocrystalline glass-ceramic composites may also provide the opportunity to tailor physical, thermal, mechanical, and optical properties for a number of applications. The

materials/compositions of this invention can be formed as a continuous film or as a powder (that can be plasma sprayed) or in a near-net shaped consolidated form. Some of the potential applications include oxidation and corrosion protection (low oxygen diffusivity and chemical durability), thermal protection for aerospace and space vehicles (high emissivity, low thermal conductivity, and low oxygen diffusivity), low observable thermally stable coatings (low dielectric constant), protection against molten metal (non-wetting character), interface coatings (non-wetting) and matrices (high strength and ease of fabrication) for ceramic matrix composites (CMCs).

A preferred method for making the composition of the present invention is described in the aforementioned U.S. Patent No. 6,036,762. An aluminum salt, such as aluminum nitrate having water of hydration is dissolved in an organic solvent, preferably an alcohol such as ethanol. A quantity of phosphorus pentoxide ( $P_2O_5$ ) is dissolved in a separate container in the same solvent. The molar ratio of Al to P in the Al solution is greater than a one-to-one ratio with phosphorus and is preferably at least 1% and most preferably at least 5% greater. The upper practical limit of excess aluminum has not been determined, but compositions containing ten times excess aluminum have been prepared, and a 1.5 to 3.5 excess molar ratio appears to be most promising in terms of retaining the amorphous content at high temperatures.

More generally, as applicable to broader aspects of this invention, this synthetic approach provides a metal phosphate precursor solution from two separate liquid components using a common organic solvent. While a variety of organic solvents may be potentially useful, liquid alcohols are preferred, such as methanol or ethanol, with ethanol being most preferred. Accordingly, a first component of the precursor solution is prepared from a metal salt dissolved in alcohol such as ethanol. A mixture of salts of different metals may be employed. Nitrates, chlorides, acetates or any salt of metal soluble in alcoholic media may be used. The choice of metal salt and/or alcohol is limited only by associated solubility considerations.

The salt of any metal may be employed in the first component. For the preparation of coatings for use in high temperature reactive environments, reference is made to U.S. Pat. No. 5,665,463, incorporated herein by reference. The metal salt may comprise a monazite having the general formula  $MPO_4$ , where M is selected from the larger trivalent rare earth elements or the lanthanide series (La, Ce, Pr, Nd, Pm, Sm, Eu,

Gd and Th). Xenotimes as described in the above patent can also be prepared. Other di- and tri-valent metals such as aluminum are especially suitable.

The second component of the precursor solution is phosphorus pentoxide ( $P_2O_5$ ) dissolved in the same solvent such as ethanol. Without limitation, there is believed a controlled reactivity between the alcohol and phosphorus pentoxide in which phosphate esters are produced. The esterification process continues, forming ester chains while the solution ages, and the solution becomes sufficiently polymeric such that good film forming properties are attained. The metal salt solution is preferably added to the phosphorus pentoxide solution shortly after preparation of the latter and before extensive esterification occurs.

The precursor solution can be prepared at a variety of concentrations, depending on the desired film microstructure. For example, using lanthanum nitrate, a solution providing up to 160 grams per liter yield of lanthanum phosphate can be obtained. The metal salt and the phosphate are provided in the mixture in either stoichiometric proportions or with an excess of metal salt to yield the desired metal phosphate.

As described more fully elsewhere, herein, the solution comprising the two components is shelf stable and can be converted to metal phosphate by heating. Since the solution has good wetting and coating properties, however, the preferred method of employment is as a coating on porous and non-porous substrates. For example, lanthanum phosphate has substantial utility as a coating on ceramic fibers, fabrics or in other structures used at high temperatures, i.e., in excess of 1200°C. The phosphate coating allows for increased toughness for the composite as referred in U.S. Pat. No. 5,665,463. The solution may be applied as a coating on non-porous materials such as metals and metal alloys.

Upon pyrolysis of the precursor coated substrate, much of the solvent evaporates at a relatively low temperature, leaving a continuous film of residual precursor material on the substrate. Upon additional heating, all species except for metal and phosphate are removed, leaving a coating of the metal phosphate. The temperature to which heating is required may be evaluated by differential thermal analysis. For the  $LaPO_4$  precursor, heating to a temperature of 600°C for a brief period assures total conversion. X-ray diffraction of the film obtained confirmed the formation of a single phase lanthanum phosphate. Scanning electron microscopy analysis of the film showed it to be smooth,

uniform, continuous and stoichiometric. The use of a volatile solvent system allows the metal phosphate to form at relatively low temperatures.

The precursor liquid can be coated onto a suitable substrate, such as a metal or alloy or ceramic or mixed with particles of ceramic material requiring oxidation and/or corrosion protection. In addition, the liquid can be drawn into fibers, placed in a mold, or used alone. Regardless, the liquid is converted into solid, stable form by annealing or pyrolysis in air. Typically, for aluminum compositions, this requires heating to temperatures normally above 750°C for a period of time, for example, for one hour, or at higher temperatures. Complete annealing becomes evident when the composition assumes a black or dark grey color.

With regard to at least the aluminum phosphate compositions of this invention, it is believed that the decomposition behavior of organic based precursor at least partially controls the molecular events leading to a unique inorganic compound. The material contains in excess of 50% of an amorphous compound and may also contain nanocrystals. The material remains amorphous and metastable when heated to temperatures from ambient and up to 1400°C or greater for extended period of time. It is believed that increased storage time of the precursor solution increases amorphous content.

Based on initial observations, it has been found that the amorphous content of the annealed composition of the present invention may be influenced by at least two factors, namely, application and age of the precursor solution. As an example of the first effect, coatings of solution applied on fibrous substrates appear to be substantially completely amorphous even after annealing at 1200°C for two hours. This has been initially confirmed by TEM analysis of solution coated and annealed on mullite-alumina fibers with an overcoat of alumina. On the other hand, powders synthesized in alumina crucibles at 1000°C for 30 minutes contain a significant fraction of AlPO<sub>4</sub> crystallites. Aging of the precursor solution appears to have a significant effect on the phosphorus environment in the precursor as well as the amorphous content in the pyrolyzed product. Storage of the solution in a refrigerator for a period of up to two years or at room temperature for over one month tends to yield more pure amorphous content.

Of the AlPO<sub>4</sub> samples tested, the composition/material had a low density in the order of 1.99 to 2.25 g/cm<sup>3</sup>, in comparison with 3.96 g/cm<sup>3</sup> for alumina. The composition

the chemical diffusivity was in the order of  $1 \times 10^{-12} \text{ cm}^2/\text{sec}$  at  $1400^\circ\text{C}$ . The material also exhibits a high emissivity, potentially useful in thermal protection systems, such as space applications. Thermal conductivity has been measured at 1 to 1.5 W/m.k. The material is inert in various harsh environments, and has a non-wetting character to most materials, including molten aluminum and solid oxides. Coatings as thin as 0.25 microns are capable of protecting metallic and other surfaces.

Potential applications include thermal, corrosion and oxidation protection for metals and metal/ceramic-based thermal protection systems, high emissivity coatings, interface coatings for silicon carbide and oxide based ceramic matrix systems, environmental barrier coatings for metal and ceramic based systems, fibers for composites and fiber lasers, corrosion protection in molten metal processing, monolithic materials for thermal insulation, catalyst supports, as well as many others. The material may also possess a low dielectric constant, making it useful in Radome applications.

#### Examples of the Invention.

##### Example 1

To make 850mL of 75.46 g/L a precursor solution to synthesize the amorphous aluminum phosphate material with a 1.75:1 Al:P ratio (.375 molar excess  $\text{Al}_2\text{O}_3$ ), 408.94 g  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in 382 ml ethanol to make 500 ml of solution. In a separate container in an inert atmosphere, 25.23 g  $\text{P}_2\text{O}_5$  was dissolved in 300 ml ethanol. After the  $\text{P}_2\text{O}_5$  is dissolved, the two solutions were mixed together and allowed to stir for several minutes. After the solution was thoroughly mixed, it was placed in a large container in an oven at  $150^\circ\text{C}$  for one or more hours. After the resulting powder is completely dried, it was annealed in air to  $1100^\circ\text{C}$  for one hour to form amorphous aluminum phosphate powder with .75 moles excess aluminum per mole aluminum phosphate.

##### Example 2

To form an oxidation resistant amorphous aluminum phosphate coating on a rectangular coupon of 304 stainless steel, the piece was dipped in the precursor solution of Example 1, diluted to a certain concentration and removed. The sample was dried in flowing air to remove the solvent. The sample was dried more thoroughly in an oven at  $65^\circ\text{C}$ . The piece was annealed in air to  $1000^\circ\text{C}$  (at a ramp rate of 10C/minute) for 100

hours and cooled to room temperature at 10C/minute, along with an uncoated piece of 304 stainless steel of the same size and shape. The weight of each uncoated piece was measured prior to anneal. The weight was measured again after coating and anneal. The amorphous aluminum phosphate coated piece showed remarkably less weight gain. The weight gain data is given in the table below.

**Table I.** Weight gain of uncoated, and coated (AlPO<sub>4</sub>, with 75% excess Al) stainless steel coupons annealed to 1000°C in air. The weight gain is related to the weight of the annealed, uncoated coupon.

<u>Sample</u>	<u>Original weight (g)</u>	<u>Weight after anneal (g)</u>	<u>Weight gained (g)</u>	<u>% Weight gained</u>
Amorphous aluminum phosphate (incl. coating)	20.3727	20.4207	0.048	0.24%
Uncoated	20.6303	22.4123	1.782	8.64%

Example 3

To form an amorphous aluminum phosphate coating on a solid substrate by plasma spray, amorphous aluminum phosphate powder made in Example 1 is milled to a small and uniform size (around 20 microns) in a ball mill. The powder is then deposited using the small particle plasma spray process (see, U.S. Patent No. 5,744,777 incorporated herein by reference in its entirety).

Example 4

Bulk amorphous aluminum phosphate is formed by electroconsolidation (U.S. Patent No. 5,348,694). Finely ground amorphous aluminum phosphate powder was mixed with a binder (1 wt% PEG 8000 and 2 wt% PEG 20M) and then pressed into a pellet. This pellet was pre-sintered at 1200°C for five hours. The pellet was then electroconsolidated at 1300°C for 30 minutes. The final pellet had a density of 1.99 g/cm<sup>3</sup>.

Example 5

Amorphous aluminum phosphate fibers were made from viscous polymer formed from the precursor solution of Example 1. The AlPO<sub>4</sub> solution was dried at 50-65°C until 40-30% of the weight is retained. The residue had a mainly clear, glassy appearance with a high viscosity. Green fibers were pulled with a needle, inserted into the viscous residue

and quickly removed. The fibers were dried immediately in flowing air at 650°F. The green fibers were then annealed to at least 900°C to form amorphous aluminum phosphate fibers.

Example 6

Rare earth and other metal ions can be incorporated into the amorphous aluminum phosphate structure. An erbium doped precursor solution with 0.75 moles excess metal (aluminum and erbium) of which 5mol% is erbium was synthesized in a manner similar to the amorphous aluminum phosphate solution of Example 1. 31.2 g Al (NO<sub>3</sub>)<sub>3</sub> 9H<sub>2</sub>O was dissolved in 75 ml ethanol. In an inert atmosphere glove box in a separate container, 1.94 g Er(NO<sub>3</sub>)<sub>3</sub> 5H<sub>2</sub>O was dissolved in 20 ml ethanol. The erbium nitrate solution was added to the aluminum nitrate solution and left to stir for several minutes. In a separate container in an inert atmosphere glove box, 3.55 g P<sub>2</sub>O<sub>5</sub> was dissolved in 40 mL ethanol. After the P<sub>2</sub>O<sub>5</sub> was dissolved, the aluminum nitrate and erbium solution was added and left to stir for several minutes. The solution was then dried at 150°C for about an hour and annealed to 1000°C for one hour. X-ray diffraction of this material annealed to 1000°C for one hour confirms the amorphous structure, with no erbium phosphate crystalline.

Example 7

Fig. 4 is a typical x-ray diffraction pattern (XRD) pattern obtained from stoichiometric aluminum phosphate synthesized from an ethanolic precursor solution containing nominal equimolar amounts of aluminum nitrate nonahydrate and phosphorus pentoxide. The solution was dried and the powder obtained was calcined to 1100°C in air for one hour and is "jet" black in color. It is immediately evident from the pattern that the material is not fully crystalline and may contain a significant amount of crystalline disorder or amorphous content. Closer examination of the broad peaks reveals the presence of disordered tridymite and cristobalite forms of AlPO<sub>4</sub>. Further annealing of this material for longer times in air (1100°C, 163 hours) does induce significant crystallization as seen in Fig. 4 where the tridymite peaks are much better defined, and the cristobalite peak is separate from the main tridymite peak.

In contrast, Fig. 5 shows the XRD pattern of aluminum phosphate synthesized with excess aluminum ( $x=.75$ , 75% molar excess) in the precursor solution. The striking difference between the patterns in Figs. 4 and 5 is immediately apparent: the diffraction

pattern for the material with excess aluminum retains broad, low-intensity peaks indicative of a large degree of non-crystalline amorphous structure and enhanced metastability.

Without restriction to any one theory or mode of operation, the precursor design, along with excess aluminum, is believed a factor in the preparation of the present compositions. The poly-esterification of  $P_2O_5$  by ethanol and hydrolysis controls the chemistry of clusters in liquid during which time a sequence of molecular events occur yielding unique spatial coordinations between P, Al, O, and -OH which is preserved through gelation and calcination. Synthesis of  $AlPO_4$  with excess aluminum significantly enhances the thermal stability of the resulting material/composition.

#### Example 8

The addition of excess aluminum to the precursor solution results in the presence of a substantial number of coordinations other than regular tetrahedral coordinations, including but not limited to distorted octahedrally coordinated aluminum, in the pyrolyzed product. Crystalline aluminum phosphate of the prior art consists of tetrahedrally coordinated aluminum and phosphorus, but  $^{27}Al$  MAS NMR of the aluminum phosphate materials/compositions of this invention shows the presence of both 4- and 6-fold aluminum (see, also Examples 35a and 35b, and Figs. 19 and 20, below) consistent with the metastability exhibited therewith.

#### Example 9

Thermal expansion of an electroconsolidated aluminum phosphate pellet was measured by dilatometry from room temperature to 1100°C (Fig. 6). The thermal expansion coefficient is considerably lower than steel which has a thermal expansion coefficient around  $13 \times 10^{-6}$  /K. But, as evident from stainless steel coating experiments, very thin coatings of such materials are able to withstand the thermal expansion mismatch and remain adherent and crack free even after heating to 1000°C and returning to room temperature.

#### Example 10

TEM analysis of a 50nm coating on Nextel 720 alumina/mullite fiber annealed to 1200°C for 100 hours shows that the aluminum phosphate composition of this invention has remained completely amorphous (Fig. 7). No nanocrystalline inclusions are evident.

Example 11

Nickel-based superalloys are frequently used in high temperature applications such as turbine blades. However, oxidation at high use temperatures is still a problem. Ni-based superalloy pieces were coated with an AlPO<sub>4</sub> material of this invention to substantially reduce the kinetics of alumina scale growth and spallation, demonstrating this invention dramatically reduces high-temperature oxidation.

Example 12

Aluminum phosphate powders synthesized as described herein can contain nanocrystalline inclusions embedded in the amorphous matrix, in contrast to completely amorphous material obtained as a thin film. TEM examination of annealed powders showed two distinct types of material. After 1 hour anneal at 1100°C, about 20-30% of the powder sample contained isolated aluminum phosphate crystallites. Most of the sample, however, contained an amorphous/glassy matrix with nm-sized crystalline inclusions that ranged from 5-30 nm (Fig. 8) and well dispersed. TEM studies of powder annealed to 1300°C for 100 hours shows that the overall fraction of nanocrystals in the material is essentially the same, with grain size increasing slightly (25-60nm).

Example 13

Similar results were obtained with ErPO<sub>4</sub> nanocrystallites in a matrix. 5mol% Er-doped powders were prepared as described elsewhere, herein. TEM analysis of Er-doped material annealed to 1000°C for 1 hour shows an increase in nanocrystalline fraction over the undoped material (Fig. 9). EDS confirms that Er is present in these nanocrystals. XRD analysis of Er-doped material annealed to 1100°C for 1 hour shows definite ErPO<sub>4</sub> peaks.

Example 14

The compositions of this invention have a low thermal conductivity (1.0-1.5 W/mK)—lower than yttria-stabilized zirconia, a commonly used thermal barrier coating material (Fig. 10). Such materials therefore show potential as providing both an environmental and thermal barrier simultaneously, and as can be achieved in application of in one coating. Thermal barrier coatings are frequently plasma sprayed, which involved partial melting of the powder. An AlPO<sub>4</sub> powder has been plasma sprayed onto steel and cast iron, and the XRD pattern does not indicate any changes in the structure.

Example 15

An AlPO<sub>4</sub> composition of this example is prepared as smooth, dense amorphous ceramic fibers, having high strength and high creep resistance in the absence of grain boundaries where flaws form easily. A high strength, creep resistant fiber stable to high temperatures would have great structural potential. (See, Fig. 11 and several other examples, below.)

Example 16

The aluminum phosphate materials/compositions of this invention are non-wetting and non-bonding. With thermal stabilities up to 1400°C, they may provide a high-temperature substitute for Teflon®-like non-stick coatings in applications ranging from cookware to engine components.

Example 17

A slurry of fine particles in solution can be applied by aerosol spraying onto a substrate. Accordingly, a slurry of AlPO<sub>4</sub> powder (average particle size = 16 microns) is mixed into an AlPO<sub>4</sub> solution in a ratio of 5g powder/100mL solution. This slurry is aerosol sprayed onto a heated stainless steel coupon. The result is a coating of AlPO<sub>4</sub> particles embedded in an AlPO<sub>4</sub> coating. The coating adheres well to the surface of the steel.

Example 18

A coating of a composition/material of this invention is obtained by chemical vapor deposition (CVD). CVD coatings can be deposited at low temperature, thereby creating an amorphous coating. CVD also allows for good stoichiometry control. Accordingly, aluminum acetylacetone and trimethyl phosphate are dissolved in toluene. This solution is placed in a liquid-delivery assisted CVD system. This liquid precursor will allow for careful mixing and stoichiometric control. The solution is transferred into a flash evaporator, where it is vaporized. This vapor enters into the reactor, and reacts and deposits as a solid on the substrate.

Example 19

Another route for the preparation of compositions of this invention can be through a reaction of a solid with a liquid phosphorus source (phosphoric acid, phosphorus pentoxide solutions, etc.). The solid may contain aluminum, which will promote the formation of amorphous aluminum phosphate. Accordingly, a solid containing a small

amount of aluminum is dipped in phosphoric acid. When this solid is heated above 800°C, the phosphorus on the surface reacts with the small amount of aluminum to form amorphous aluminum phosphate.

Example 20

Composite coatings of this invention can be deposited on a substrate. Solid particles are added to an AlPO<sub>4</sub> solution to form a slurry. This composite coating can be deposited on a substrate by dip coating, applying with a brush, aerosol spraying, etc. When this coating is fully formed under a heat lamp or in a furnace, a composite coating, containing particles embedded in an AlPO<sub>4</sub> coating is produced. The particles can be of any composition.

Example 21

Glasses are susceptible to corrosion in a variety of atmospheres, from distilled water to humid air. Sodium silicate glass is a common glass and is very susceptible to corrosion whether the glass is immersed in liquid, being rained on, or simply being stored in a humid warehouse. Glass containers are susceptible to corrosion from the liquid they are containing. Water and acidic and basic media promote corrosion of glass. Glass windows are subject to corrosion when it rains. Glass that is being stored is subject to localized pitting as atmospheric humidity deposits as drops on the surface.

Through an ion exchange reaction with hydrogen ions, the sodium ions dissolve into the surrounding water. The hydroxyl content in the water dissolves the silica as well, but this process is much slower.

Several methods of combating glass corrosion are used. Some common methods of increasing durability of commercially produced glasses include: the addition of other components to the melt and forming a protective coating. CaO, Al<sub>2</sub>O<sub>3</sub> and MgO are commonly added to the sodium silicate melt to retard leaching of the sodium. Surface coatings are provided by treatment with SO<sub>2</sub> gas to form sodium sulfate and annealing the glass in a trace fluorine atmosphere.

The compositions/materials of this invention provide a transparent coating on glass. The coating goes down very smoothly, and the coating is only readily visible in areas where it has been disturbed (such as where it was held during dip-coating). Such coatings could be used to increase chemical durability without decreasing transparency.

This invention could provide a protective layer, which limits the transport of hydrogen or hydroxyls to the glass surface, and the transport of the corrosion products out of the glass.

Example 22

Aqueous solutions of this invention are desired as a non-flammable, non-toxic alternative to their alcoholic counterparts. Aqueous solution does not require special hazardous labeling during shipping, does not require the large amount of ventilation in the workplace, and is more attractive to manufacturers accustomed to working with aqueous systems and processes. Dried AlPO<sub>4</sub> gel was produced by heating solution at 100°C in a convection oven. This dried gel is white and fluffy. This gel was dissolved into deionized water. The gel goes into solution easily, forming a viscous, yellowish solution. When annealed to 1100°C for 1 hr, the XRD pattern shows the typical aluminum phosphate diffraction pattern. When annealed to 1000°C for ½ hr, the XRD pattern showed an amorphous hump, that is typical of an aged composition/material. The powder is jet black and glassy in appearance.

An aqueous solution can be made much more concentrated: up to 25% by weight AlPO<sub>4</sub> versus 10-15 wt% in ethanol. This solution was coated onto a glass slide by standard dip coating. A concern with aqueous solutions is that the film formation characteristics are different and preparation of a continuous, smooth film may be more difficult than through use of an alcoholic solution.

Example 23

With reference to the preceding discussion regarding precursor solutions, a viscous, clear liquid can be prepared from which fibers can be pulled by inserting and retracting a needle. The fiber precursor is made by concentrating precursor solutions in a rotary evaporator to approximately 30wt% concentration. The fiber precursor can be difficult to prepare at the risk of becoming too concentrated. The fiber precursor is unstable on its own. After concentration, a clear liquid is left. This liquid is stable for 10 minutes – hours, but will eventually spontaneously decompose in a strong exothermic reaction. The resulting fiber precursor can be used, but there is generally a lot of foam. However, if the solution is put in a water bath immediately after removing it from the rotary evaporator, it keeps the decomposition from proceeding so violently, and a clear, slightly yellow liquid results. Accordingly, 100mL of 9.1 wt% solution is condensed to 40mL in a rotary evaporator. The temperature was 60°C, and the pressure was varied to

keep the ethanol evaporating. After the solution was concentrated, it was poured into a jar and kept in a water bath to sit. After 15 minutes, the decomposition started, and clear, viscous, yellow liquid remained.

#### Example 24

Intended fiber applications include a) structural ceramic fibers used in ceramic matrix composites, metal matrix composites—currently, SiC and a variety of oxide fibers are being developed, b) fiber-optic amplifiers, and c) fiber lasers. Fibers have been hand-drawn from fiber precursor (for scale-up, the precursor will be fed into a spinnerette to produce continuous single or multi-filaments (typically 10 microns in diameter. The fibers are drawn by putting a thin rod into the precursor, then quickly withdrawing it. The resulting fibers are smooth and dense. The diameter is not uniform, but due only to the hand drawing process. The fibers show stability up to 10 hours at 1200°C, but after 100 hours at 1200°C, dramatic phosphorus loss is seen. An attractive advantage of such fibers will be the use of nanocrystalline inclusions within the amorphous matrix to improve its strength, toughness, creep resistance, and thermal expansion properties. Accordingly, a small metal spatula is immersed slightly in the precursor from the preceding example. The spatula is withdrawn at a steady rate, and the fiber is caught on a piece of stainless steel mesh. The mesh is bent into a C shape, so the fiber was touching the steel at only 2 points. The fibers were put in a furnace and annealed in air at 900°C for 30 minutes.

#### Example 25

Films can be produced by dip coating onto a variety of substrates, steel being the most common. The sample is air dried, and then heated with an infrared lamp to cure the coating. The coating cures much more quickly than in the furnace, 30 sec to 3+ minutes depending on the substrate. This eliminates the step of putting the sample in the furnace and reduces substrate temperature and heating times. Species removed from the precursor state in order of their volatility are ethanol and other hydrocarbons (below 100°C), nitrates (typically above 500°C), and hydroxyls (at least above 1000°C in case of powders). For very thin films (below 500 angstroms), the temperature limits may be much lower. It is worth noting that the exothermic peak in the DTA around 225°C suggests formation of the amorphous phosphate phase. Accordingly, a piece of stainless steel is half-dip coated in precursor solution. The piece is heated with the IR lamp for

2 minutes. The resulting piece shows the bottom half well-coated and the top half still appears as it did previously. In contrast, when stainless steel is half-dipped and annealed in the furnace, the bottom half shows a good compositional coating, but the whole piece is slightly discolored from oxidation.

#### Example 26

The compositions of this invention have been spin coated onto silicon and steel in a standard spin coater. Aluminum phosphate prepared as described herein has also been coated in a 3-dimensional process onto steel by immersing the piece and removing it, then spinning the whole piece (e.g., use of a drill press). The coatings seem to be more uniform and have fewer cracks than standard dip coated pieces. Accordingly, a piece of stainless steel is immersed completely in a 6.6 g/L aluminum phosphate solution. The piece is withdrawn, and immediately spun (rpm to be determined, but less than 540). The piece is cured with the IR lamp. The piece is cured slowly by slowly bringing the IR lamp closer to the piece, over a period of 5 minutes.

#### Example 27

Because  $P_2O_5$  is very hygroscopic, preparation is best carried out inside an dry glove box. To test the possibility of working in the open atmosphere, the  $P_2O_5$  was weighed outside the glove box and left to sit overnight. Overall, the  $P_2O_5$  picked up 3.8 g of water from an original 19g  $P_2O_5$ . This syrupy  $P_2O_5$  was dissolved in ethanol, and an aluminum nitrate solution was added. The XRD pattern shows the desired aluminum phosphate composition after 1100°C 1h anneal, proving it can be synthesized in ambient atmospheres without using controlled environment, thus reducing the need for expensive atm control. Accordingly, 19.57g  $P_2O_5$  is weighed out and left to sit in the laboratory and was left for 22 hours, taking up water to provide a syrupy consistency, instead of powder as it is when it is dry. This was dissolved in ethanol and added to aluminum nitrate solution. The XRD shows the resulting aluminum phosphate after 1100°C, 1 hr anneal.

#### Example 28

Composition of this invention can be applied to glass by a dip coating process. The resulting coating is very smooth and transparent. Where the coating is continuous, it is featureless under the optical microscope, and is only noticeable when held up to the light. Coatings on glass are needed for corrosion protection, as a glass-strengthening aid (heal surface flaws), and for altering optical properties. Accordingly, a glass microscope

slide is dipped in a 17.6 g/L solution. The piece is blow dried with cold air until dry. A low power IR lamp provides gentle heat. After it is dry, the high power IR lamp is turned on and the piece is heated for 4 minutes.

#### Example 29

Dip coated silicon can be annealed 1200°C, for extended periods of time. Coatings on silicon may be useful in the semiconductor industry as a low dielectric stable coating (dielectric constants lower than 2.9 is desired); a typical aluminum phosphate powder of this invention with dielectric constant as low as 3.3 has been made; further optimization may even lower it further to meet the 2.9 criteria, providing an inexpensive way to make these coatings and achieved such results. Accordingly, a piece of silicon was dip coated and annealed at 1200°C for 180 hours. There is evidence of some coating degradation, as there is no phosphorus evident in the TEM cross-section. Similar techniques can be used to coat molybdenum substrates.

#### Example 30

Solution of the present invention can be spray dried. The resultant particles had a mean diameter of 11.5 microns and were generally between 5-25 microns. Powders annealed at 1100°C, 1 hr retained the characteristic spectral patterns.

#### Example 31

It has been determined that the Raman peaks at 1350 and 1600  $\text{cm}^{-1}$  are related to elemental carbon. It was also determined that the peak near 1350  $\text{cm}^{-1}$  in some FTIR spectra showed was the result of atmospheric contamination, not P=O. The presence of nanoinclusions of carbon is believed responsible for the black color of the powders of this invention. Nanocrystalline carbon (with a grain size as small as 15Å) shows peaks at 1350 and 1600  $\text{cm}^{-1}$  in the Raman spectrum. Carbon has a weak IR spectrum, which explains why there are no carbon peaks in the FTIR.

XPS analysis was performed on annealed powders. Both as-annealed specimens and crushed powders (to expose fresh surfaces) were analyzed by Physical Electronics Corporation (MN, USA). The as-annealed specimens showed carbon content of less than 0.1 % whereas the crushed powders did show carbon presence near 1.6%. However, the report cast doubt on the 1.6% for the crushed powder. The skepticism was based on powder dispersion in the chamber, and may be the result of some surface contamination not removed during extensive sputtering to remove 1500Å of the surface from the

crushed powder (500Å was removed from the as-annealed powder to remove surface contamination that was reported to be typical for any material exposed to air). This assessment was also supported by TEM and SEM analysis with low Z detectors, although the detection limits with energy dispersive spectra (EDS) are generally above at least 1 wt %. In addition, no graphite inclusions have been observed within the amorphous matrix. It is indeed possible that the size of these inclusions are below 5 nm and are randomly distributed or that it is present in a glassy form mixed in with the amorphous oxide matrix.

Both Raman spectroscopy and CHNS (Carbon-Hydrogen-Nitrogen-Sulfur) analysis have confirmed the presence of carbon in the aluminum phosphate materials of this invention. The amount of carbon present is indicated by the color of the powder. Black powder contains more carbon than lighter powder. Even powders described as "gray" or "light" are not truly gray, they are a mixture of black and white domains that appear gray when crushed.

A pellet of the black composition/powder was sent to Oak Ridge National Lab for testing in the "Kaiser rig." The pellet was annealed at 1200°C for 500 hours in a total pressure of 10 atmospheres, with 15% steam. The pellet lost approximately 5wt% during the experiment, but otherwise appeared intact. The pellet was almost completely white. The surface was removed to eliminate effects of any surface contaminants and the pellet was x-rayed. The X-ray diffraction pattern was similar to the original powder (Fig. 12). The XRD pattern did not indicate significant crystallization. When observed under the optical microscope, the pellet had a few isolated black grains, but was over 98% white.

TEM analysis of the crushed pellet indicates that there are nanocrystalline inclusions embedded in an amorphous matrix (Fig. 13). Electron diffraction patterns show diffuse amorphous rings superimposed on spot patterns, which is typical for the compositions of this invention.

Raman spectra were taken. The microRaman used has a spatial resolution of approximately 3-5 microns, so spectra could be taken of black and white domains in the same sample. Black areas consistently showed peaks near 1350 and 1600  $\text{cm}^{-1}$ . The intensity of these peaks scaled with each other from sample to sample. White areas showed low intensity peaks which lined up with crystalline berlinit, and did not show the peaks at 1350 and 1600  $\text{cm}^{-1}$  (Fig. 14).

Further analysis is pending, but the results of this example are encouraging for use of this invention in steam environments including its use as an environmental barrier coating in SiC-based composites used in coal combustion applications where low oxygen diffusivity combined with resistance to high temperature steam are critical needs. In addition, use of such coatings for steam-laden atmospheres for mid-high T applications (such as petrochemical processing) are also relevant.

To illustrate the results of this example and just one application of the present invention, there is a need make coal-fired power generation more energy efficient by increasing the combustion temperature. Greater efficiency of power generation will help alleviate increasing demand for power and reduce both solid and gas phase hazardous waste products. As is demonstrated in the state of California recently, power demand is increasing dramatically. California has been faced with rolling blackouts which have cost millions of dollars for businesses located there. Certainly, more efficient power generation plants are necessary to offset the increasing demand with limited environmental impact.

Currently, the temperatures in the boiler are 550-650°C. Commonly used alloys do not have the required properties for use at 700°C and above. The specifications required for next-generation Ultra-Supercritical Boilers are high creep rupture strength at 750°C, and high corrosion resistance, with the loss of no more than 1mm in cross-section after 100,000 hours of service. Austenitic stainless steels are desirable as a replacement material because they are inexpensive and can maintain necessary strength at high temperatures. However, these alloys encounter problems both with high temperature oxidation and sulfidation and corrosion by coal ash. There is also a problem with coal ash erosion of steel parts. However, the coal ash quickly coats the parts and, in effect, forms a protective layer on the substrate.

Over the past decades, extensive R&D has been conducted on protection of metals and alloys in coal combustion environments. Many new alloys have been developed, along with coatings to slow the rate of degradation. Researchers have explored the corrosion resistance of commercial stainless steels, modified stainless steels, nickel-base alloys and others. Ferritic stainless steels corrode by the formation of  $\text{FeSO}_4$ . They have found that nickel and cobalt containing alloys corrode easily because of the ease of formation of  $\text{NiSO}_4$  and  $\text{CoSO}_4$ . Both of these sulfates form a low-melting eutectic with

$\text{Na}_2\text{SO}_4$ , increasing the corrosion of the alloy. High chromium content alloys (greater than 25%) show improved corrosion resistance, because a chromia scale grows from oxidation. However, these alloys are subject to corrosion as well, which is most severe at intermediate temperatures where the chromia grows slowly. The sulfur present in the combustion gas forms  $\text{CrS}_2$  which degrades the quality of the oxide scale, further reducing its effectiveness as a protective coating. In response to these problems groups have added other alloying elements to the steels, such as tantalum and niobium which have increased corrosion resistance. Aluminum containing alloys and intermetallics ( $\text{Fe}_3\text{Al}$ ) have been applied in hope of developing an aluminum oxide scale which shows superior oxidation and corrosion protection. However, these high-tech alloys and most coatings are prohibitively expensive for widespread use.

A suitable system which attains the necessary specifications at a reasonable cost for use for general power plant use has heretofore not been found. An ideal solution to this problem would be an inexpensive coating that would serve as an oxidation and corrosion barrier for a common austentic steel. The present invention provides an inexpensive material that can be applied very easily, and would be a low-cost solution to the problem. If the temperature of the plant can be increased, the efficiency will also increase, leading to benefits of increased output power for a given amount of coal, which will give lower-cost energy, and environmental benefits of having to burn less coal. This not only saves money in processing power, but also reduces clean-up costs, which can be substantial. The compositions are inexpensive and easy to apply: spraying a solution onto the exterior of a heat exchanger tube or inside a boiler, for example.

#### Example 32a

$^{31}\text{P}$  NMR spectra of a precursor solution for a preferred aluminum composition shows that the aluminum nitrate is interacting with the phosphorus pentoxide solution to form one or more unique complexes. For basis of comparison, the  $^{31}\text{P}$  NMR spectrum of phosphorus pentoxide in ethanol is presented. Fig. 15a shows the spectrum of  $\text{P}_2\text{O}_5$  dissolved in ethanol, and was taken shortly after dissolution. Fig. 15b shows the same solution after 24 hours of reflux.

#### Example 32b

The addition of aluminum nitrate  $\text{Al}(\text{NO}_3)_3 \bullet 9\text{H}_2\text{O}$  to the phosphorus precursor solution of Example 32a changes the  $^{31}\text{P}$  spectrum significantly. Figs. 16a-b show three

spectra from three admixed precursor solutions: the bottom curve is from C-1 (stoichiometric Al), and the other two are for increasing aluminum addition (C-1.5, 50% excess Al; and C-2, 100% excess Al). The differences between these spectra and the spectra shown in Fig. 1 are readily apparent.

A set of new peaks appears between [-15 and -24 ppm]. None of these peaks are observed in the  $P_2O_5$  + ethanol precursor spectra. These peaks are believed due a complexation of the aluminum with the phosphorus species. A pattern is observed upon increase of Al content from stoichiometric to a 2-fold excess.

#### Example 33

The solutions of Example 32b were annealed to high temperature (1100°C) for long times (160 hrs.). The stoichiometric composition becomes somewhat crystalline over time, while those materials of this invention with excess aluminum provide XRD patterns showing substantial amorphous character—denoting enhanced metastability. (See, Figs. 17a-b.)

#### Example 34

FTIR spectra of annealed materials/compositions of this invention show several unique features. For short anneal times (1hr) both stoichiometric ( $x = 0$ ) and non-stoichiometric ( $x = 0.25, 0.5$  and  $0.75$ ) compositions show similar features. The spectra are shown in Fig. 18. The spectra show predominately Al-O-P bonds, but show some features attributed to Al-O-Al and P-O-P. The Al-O-Al seems to be present in increasing amounts with increasing aluminum content. Stoichiometric compositions contain a very small amount of Al-O-Al. Stoichiometric compositions show a fairly strong P-O-P feature, which is smaller in  $Al:P = 1.25$ , and is very small (or nonexistent, it is hard to be certain) in  $Al:P = 1.5$  and does not show up in  $Al:P = 1.75$ .

#### Example 35a

Stoichiometric compositions show distortion in the aluminum coordination after 1100°C, 1 hr anneal. Fig. 19 shows a deconvolution of this spectrum. There are four curves in the deconvolution spectrum which add to the complete spectrum. The sharp peak near 39 ppm indicates Al in regular tetrahedral coordination. The other peaks indicate aluminum in distorted coordination and are listed in Table II.

Table II. Deconvolution of  $^{27}\text{Al}$  NMR spectrum of stoichiometric  $\text{AlPO}_4$ .

tetrahedral peak position	octahedral peak position	relative area
38.163		100
33.222		45.52
	10.749	11.11
	-16.356	14.84

Example 35b

Deconvolution of the  $^{27}\text{Al}$  MAS NMR spectrum for a non-stoichiometric composition ( $x = 1.0$ ) shows there are distorted 4-fold aluminum species, along with more regular 4-fold aluminum (Fig. 20.) The peak near 40 ppm is tetrahedral aluminum, and the peak fit highlighted in green shows regular coordination, while the peak highlighted in red shows aluminum in distorted octahedral coordination. The regular 4-fold aluminum is believed present in the nanocrystals while the distorted 4-fold and 6-fold aluminum is present in the amorphous matrix. Table III shows the relative peak positions and areas attributed to tetrahedral and octahedral aluminum.

Table III.

octahedral peak position	tetrahedral peak position	relative area
-9.37		15.667
7.027		26.06
	38.847	100
	40.206	43.13
	62.638	11.9

**CLAIMS**

1. A high temperature stable composition comprising aluminum phosphate wherein the ratio of aluminum to phosphorus is greater than one-to-one, said composition characterized by containing at least 50 percent by weight of an amorphous content, said composition being metastable of temperatures from ambient up to 1400°C.
2. The composition of Claim 1 additionally comprising a substrate, said composition being a coating on said substrate.
3. The composition of Claim 1 wherein said composition is in the form of a fiber.
4. The composition of Claim 2 wherein said coating protects said substrate from oxidation at elevated temperatures.
5. The composition of Claim 2 wherein said coating protects said substrate from corrosion at elevated temperatures.
6. The composition of Claim 1 comprising an additional metal.
7. An aluminum phosphate composition, said composition comprising aluminum phosphate wherein the amount of aluminum relative to phosphorus in said composition exceeds five percent, said composition being metastable at temperatures up to 1400°C.
8. A method for protecting a substrate from corrosion and oxidation at elevated temperatures, said method comprising the steps of applying a precursor solution to said substrate, said precursor solution comprising phosphorus pentoxide and an aluminum salt, wherein the ratio of aluminum to phosphorus is greater than one to one, and thereafter drying annealing said solution on said substrate.

9. A metastable material comprising an aluminum phosphate composition having the formula  $Al_{1+x}PO_{4+3x/2}$ , wherein x is about 0 to about 1.5, said composition having structural components absorbing radiation in the infra red spectrum at about  $795\text{ cm}^{-1}$  to about  $850\text{ cm}^{-1}$ , said components present at temperatures of at least about  $1000^{\circ}\text{C}$ .

10. The material of claim 9 wherein x is about 0.

11. The material of claim 10 wherein x is about 0.1 to about 1.0.

12. The material of claim 11 wherein said material is substantially amorphous.

13. The material of claim 11 wherein said material is metastable at temperatures at least about  $1200^{\circ}\text{C}$ .

14. The material of claim 11 further including crystalline particles.

15. The material of claim 14 wherein said crystalline particles are  $ErPO_4$ .

16. A method of using an aluminum phosphate composition to enhance substrate oxidation resistance, said method comprising:

    providing an aluminum phosphate composition, said composition having the formula  $Al_{1+x}PO_{4+3x/2}$ , wherein x is about 0 to about 1.5; and

    applying said composition to a substrate.

17. The method of claim 16 wherein said composition is annealed prior to said application.

18. The method of claim 16 wherein said composition is annealed after said application.

19. The method of claim 16 wherein said composition is dip-coated onto a substrate.

20. The method of claim 16 wherein said composition is plasma-sprayed on a substrate.

21. The method of claim 16 wherein said composition is aerosol-sprayed onto a substrate.

22. The method of claim 16 wherein said composition is a slurry in a solution of a compositional precursor.

23. A method of using the aluminum content of an aluminum phosphate material to affect the metastability of said material, said method providing an aluminum phosphate material using an aluminum salt precursor compound, said material having an aluminum content corresponding to the aluminum content of said precursor compound, said precursor compound and said material aluminum content sufficient to provide a material metastability.

24. The method of claim 23 wherein said material aluminum content is stoichoimetric.

25. The method of claim 23 wherein said material aluminum content is greater than stoichoimetric.

26. The method of claim 23 further including a second component selected from the group consisting of silicon, lanthanum and zirconium.

27. An aluminum phosphate product having Al-O-Al structural moieties absorbing radiation in the infra red spectrum at about  $795\text{ cm}^{-1}$  to about  $850\text{ cm}^{-1}$ , said product obtainable by mixing an alcoholic solution of phosphorus pentoxide with a solution of an aluminum salt, and heating the admixture.

28. The product of claim 27 wherein said product is substantially amorphous.
29. The product of claim 27 further including crystalline particles.
30. The product of claim 29 wherein said particles are crystalline  $\text{ErPO}_4$  inclusions prepared by incorporating an erbium salt with said aluminum salt solution.
31. The product of claim 27 further including metal oxide particles, said particles selected from the group consisting of Group IIIA and IIIB-VIB metal oxides, said particles in an amount sufficient to modify the thermal expansion coefficient of said product.

Fig. 1

1/14

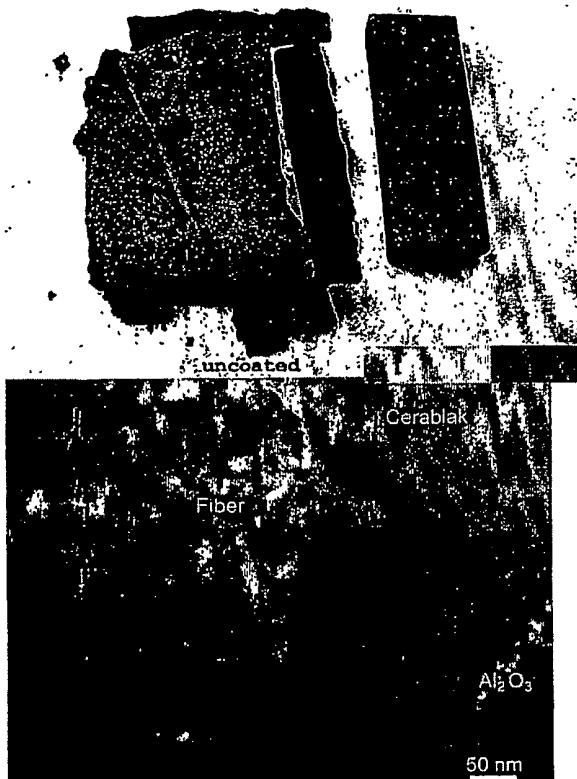


Fig. 3

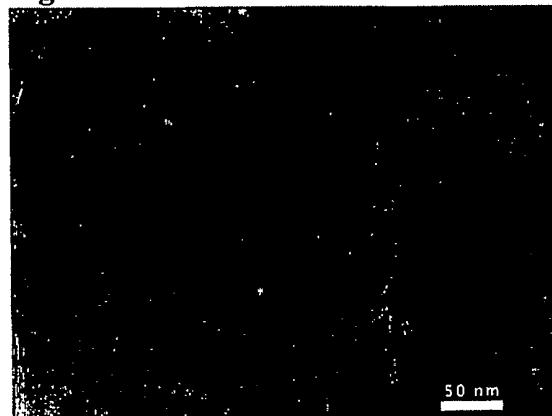


Fig. 2a

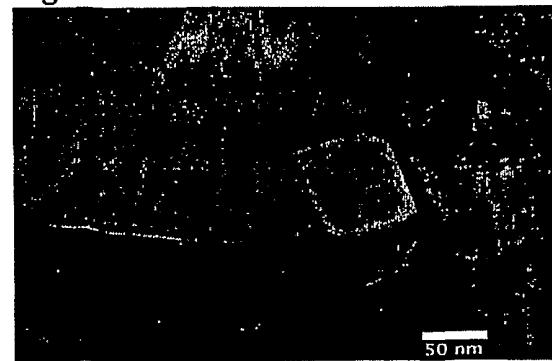


Fig. 2c

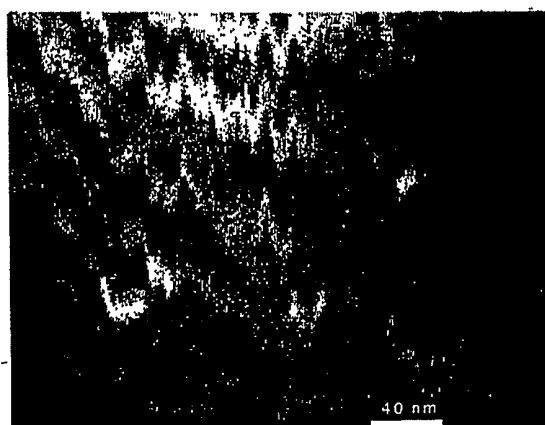


Fig. 2b

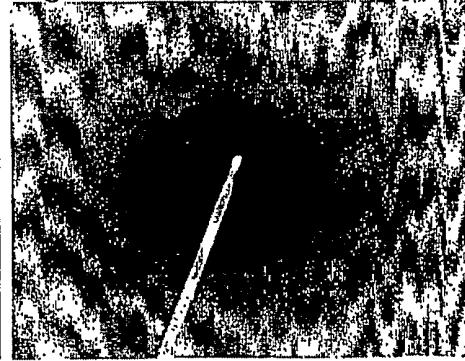


Fig. 2d

2/14

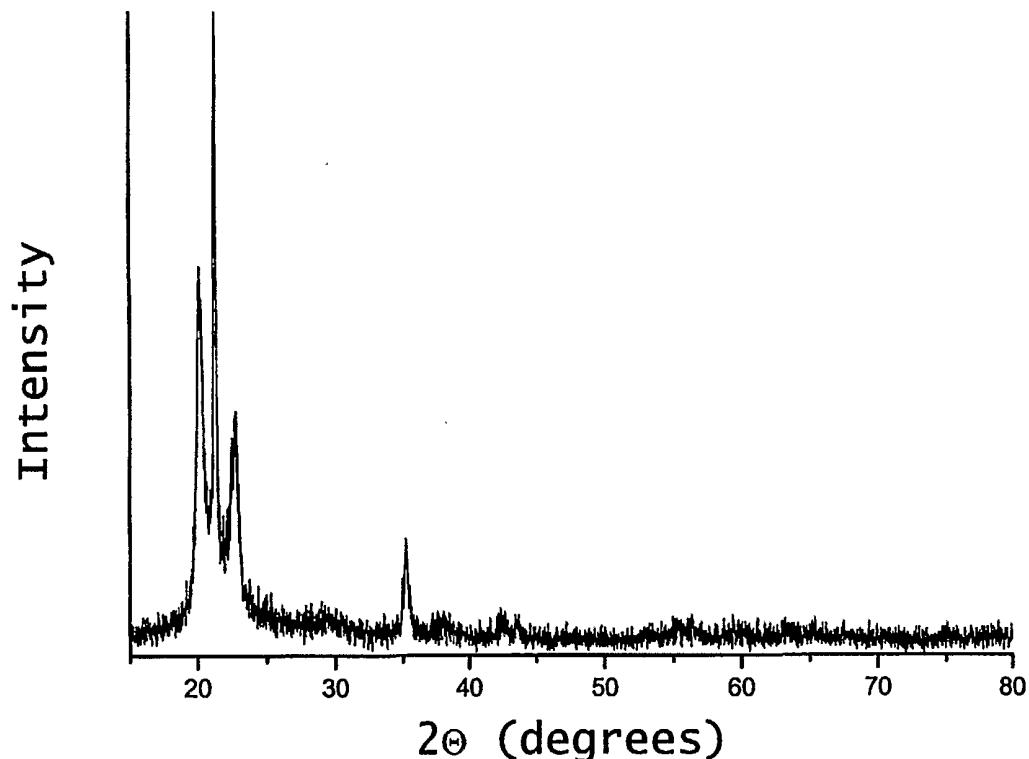


Fig. 4a

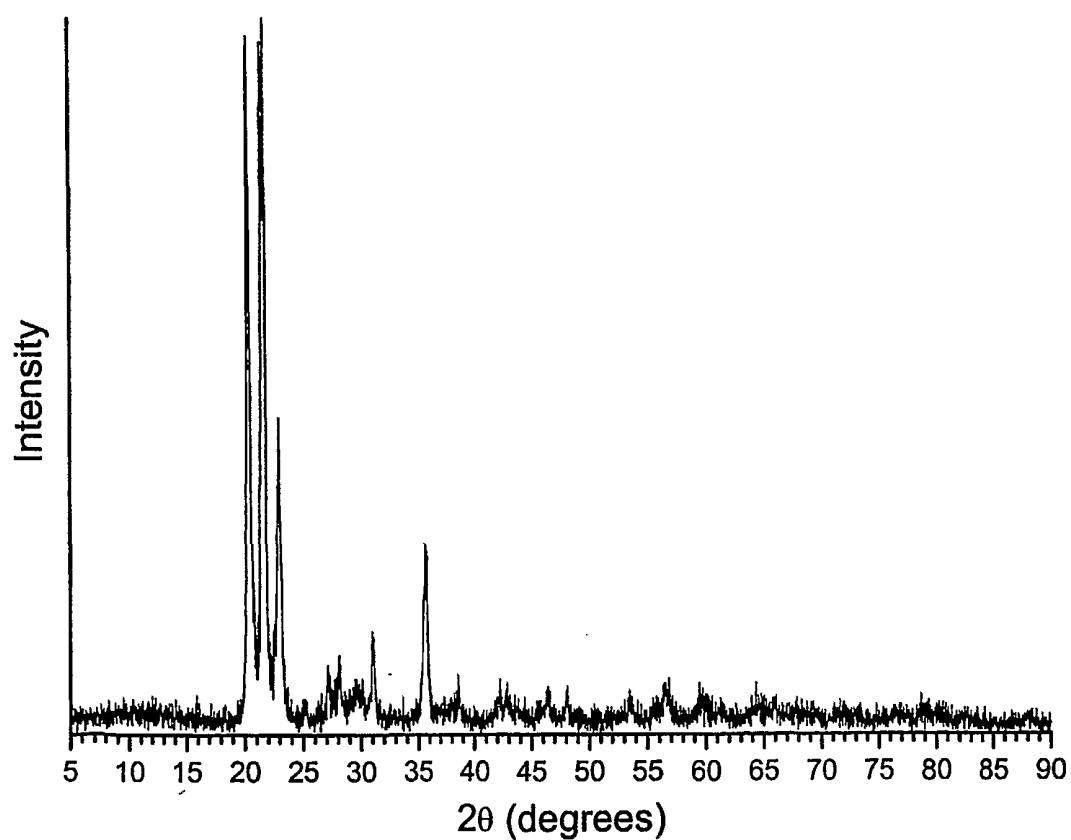


Fig. 4b

3/14

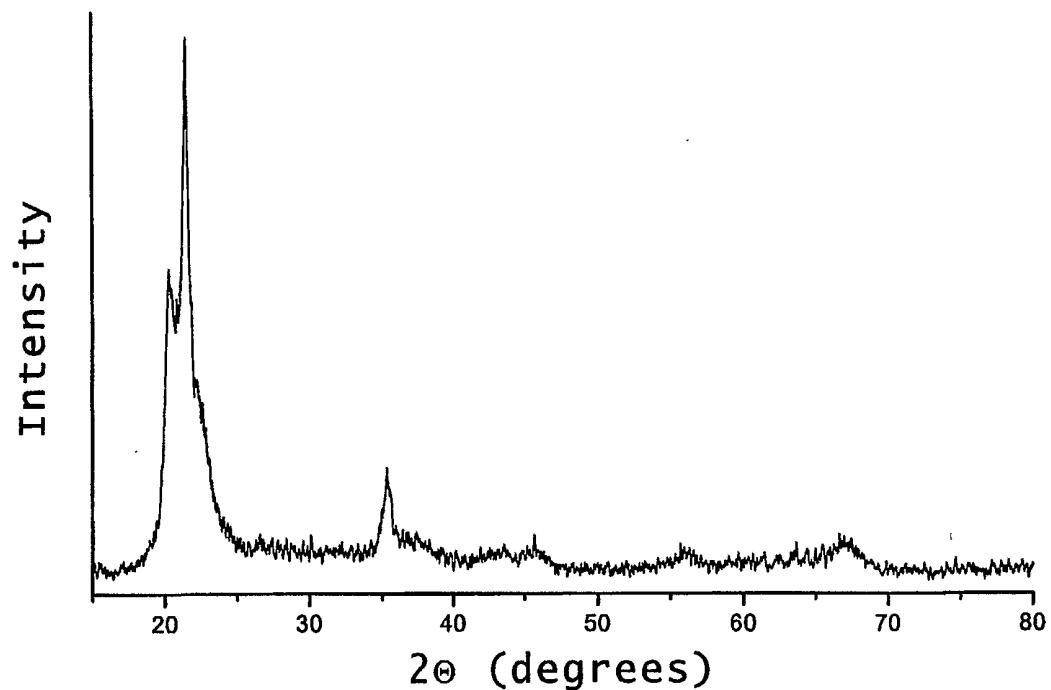


Fig. 5a

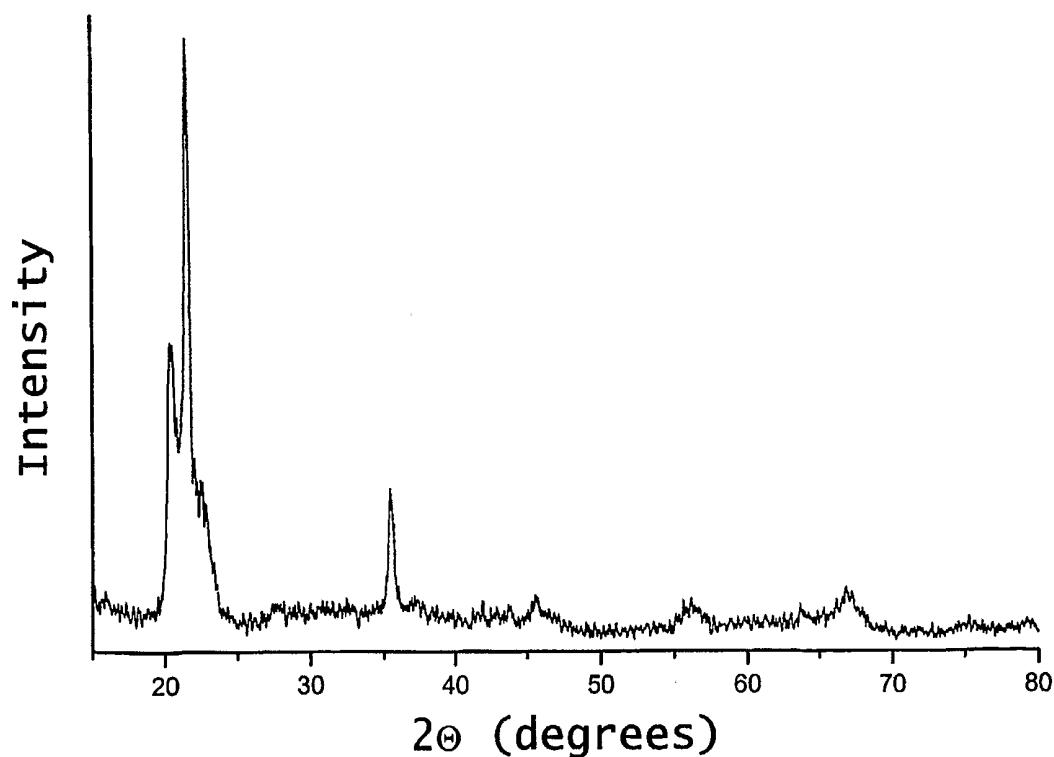


Fig. 5b

4/14

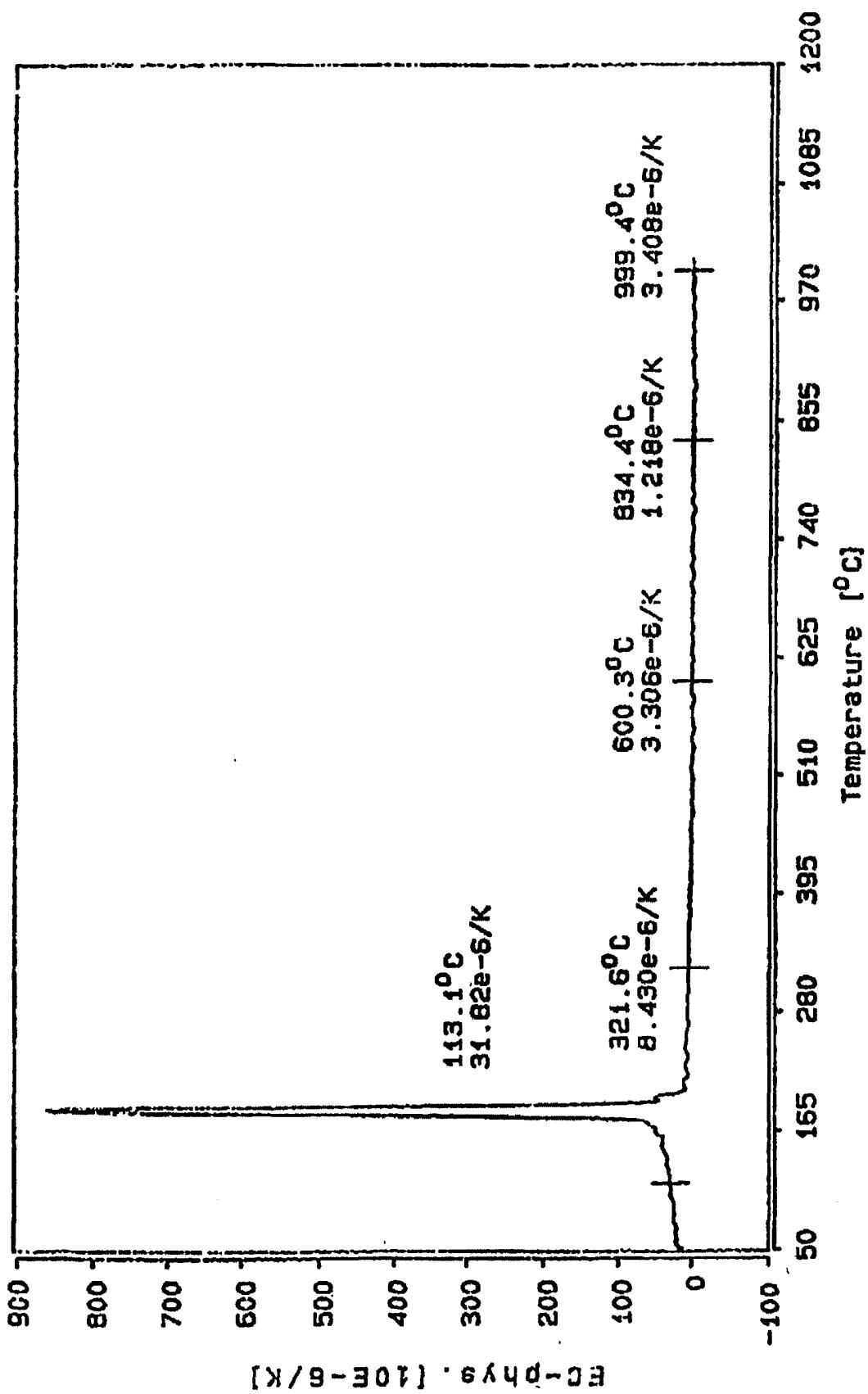


Fig. 6

5/14

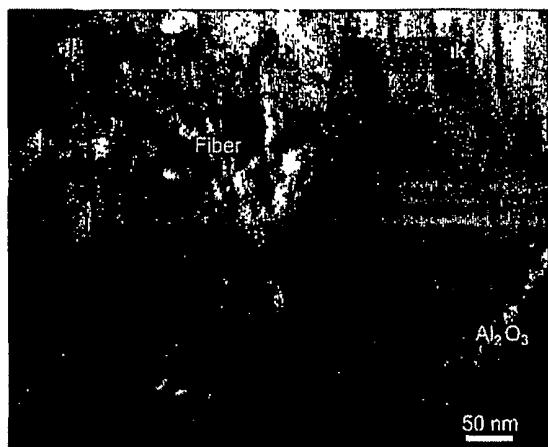


Fig. 7a

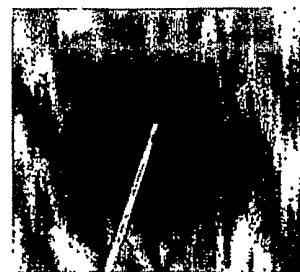
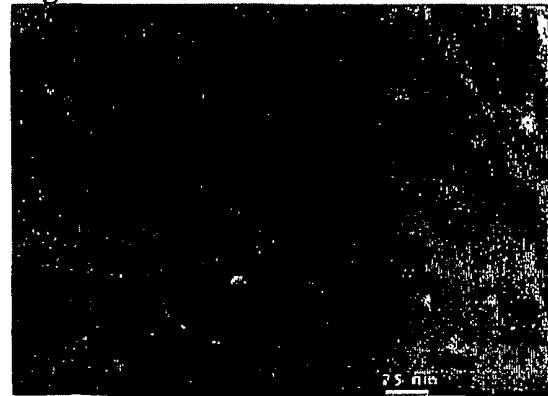


Fig. 7b

Fig. 8



Fig. 9



6/14

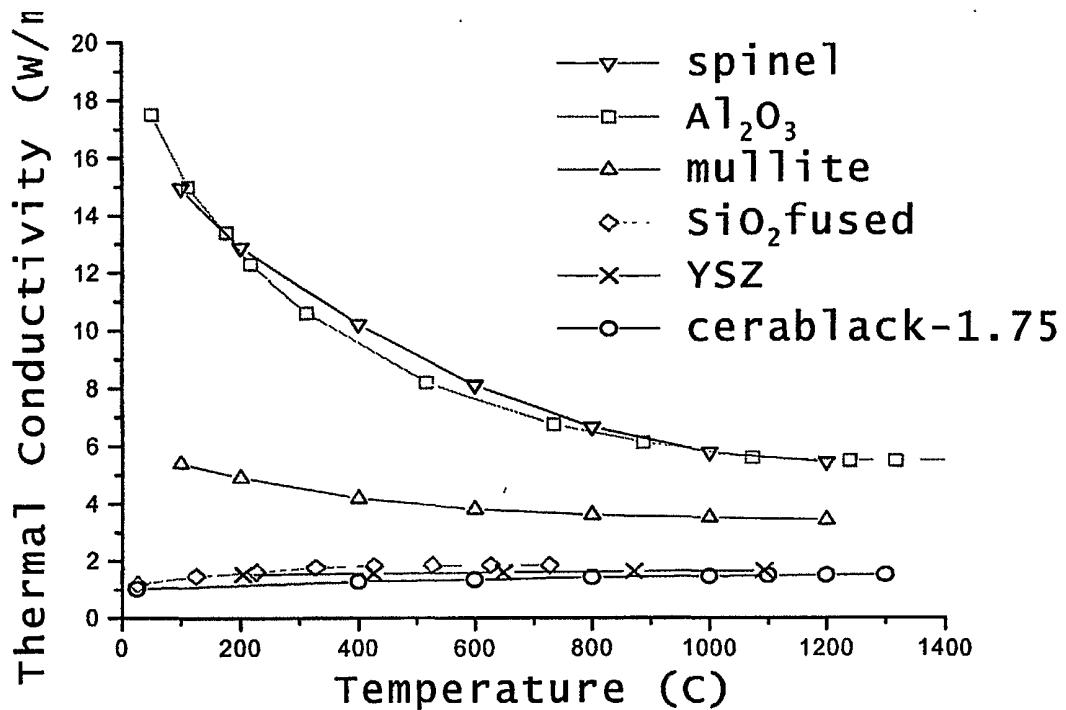


Fig. 10a

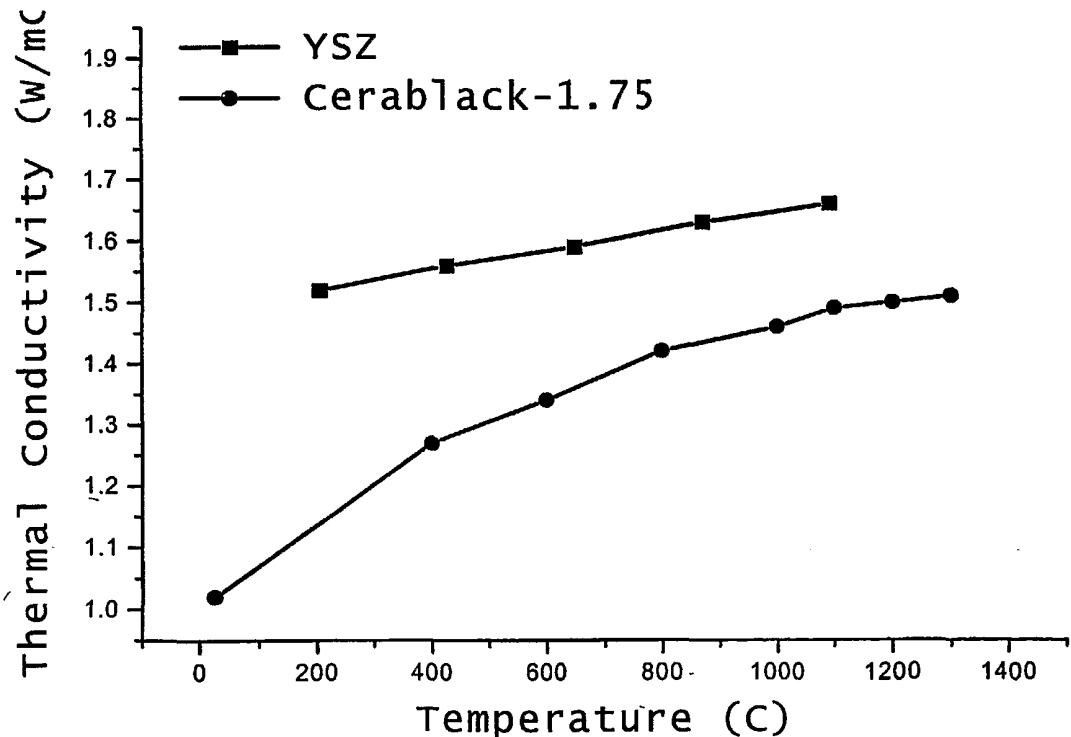
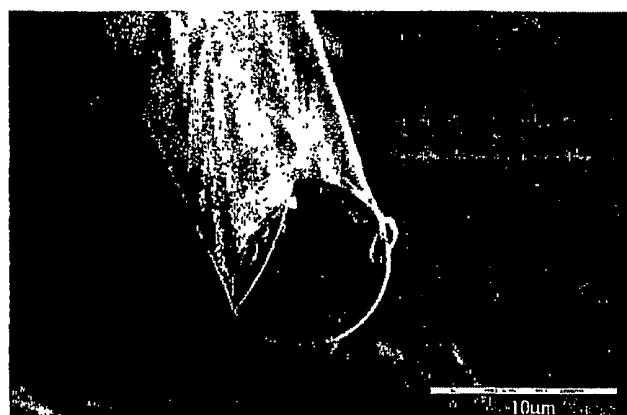
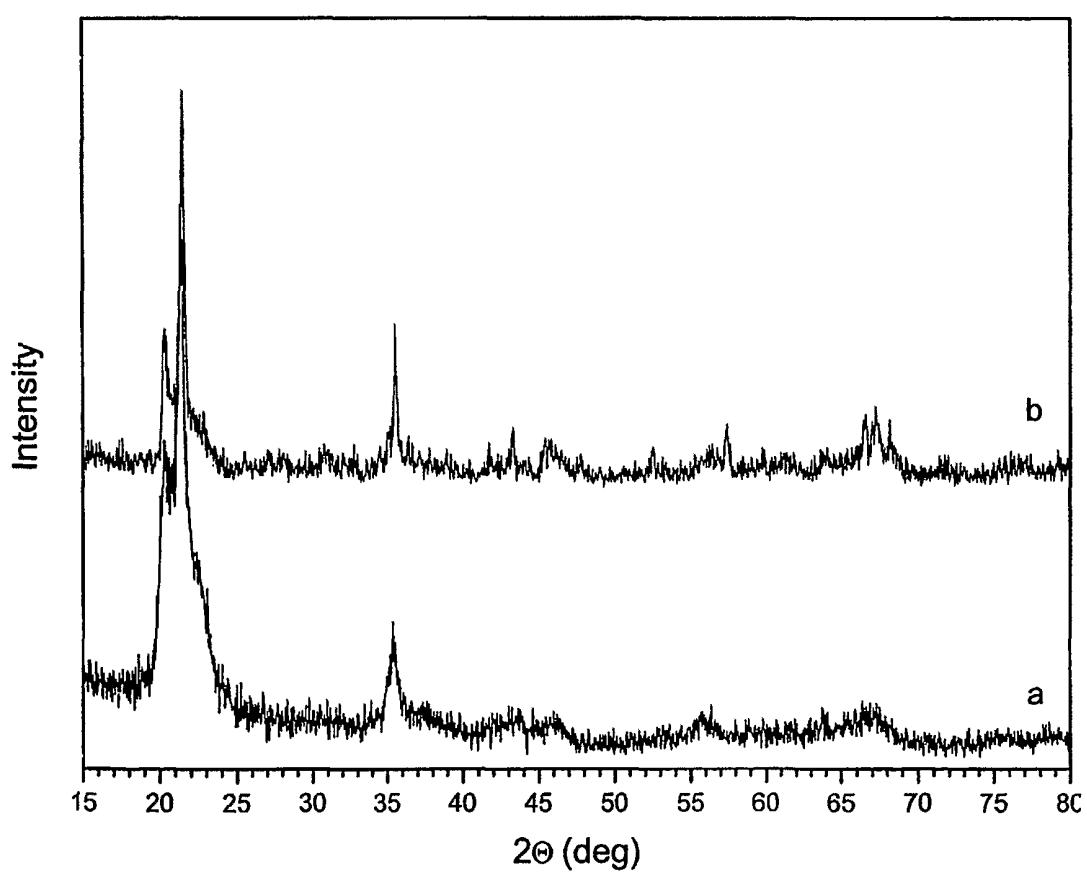


Fig. 10b

7/14

**Fig. 11****Fig. 12**

8/14



Fig. 13a

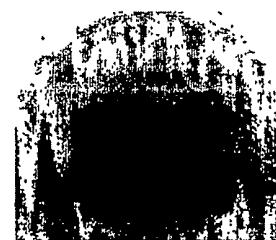
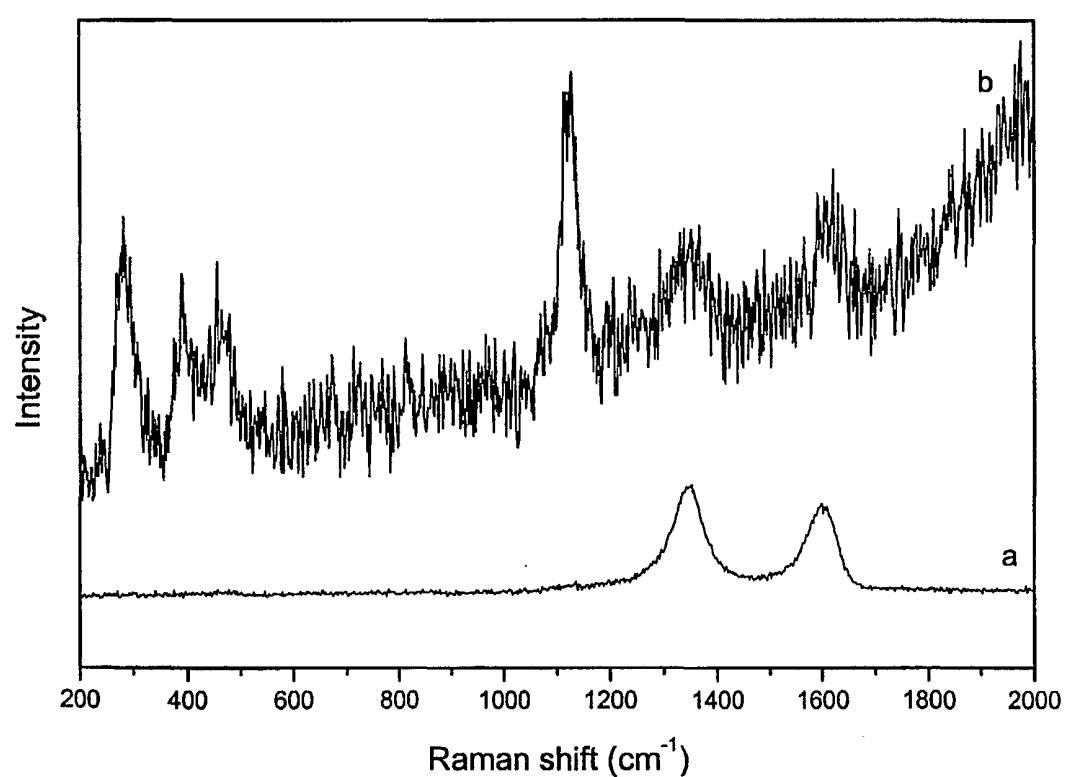


Fig. 13b

Fig. 14



9/14

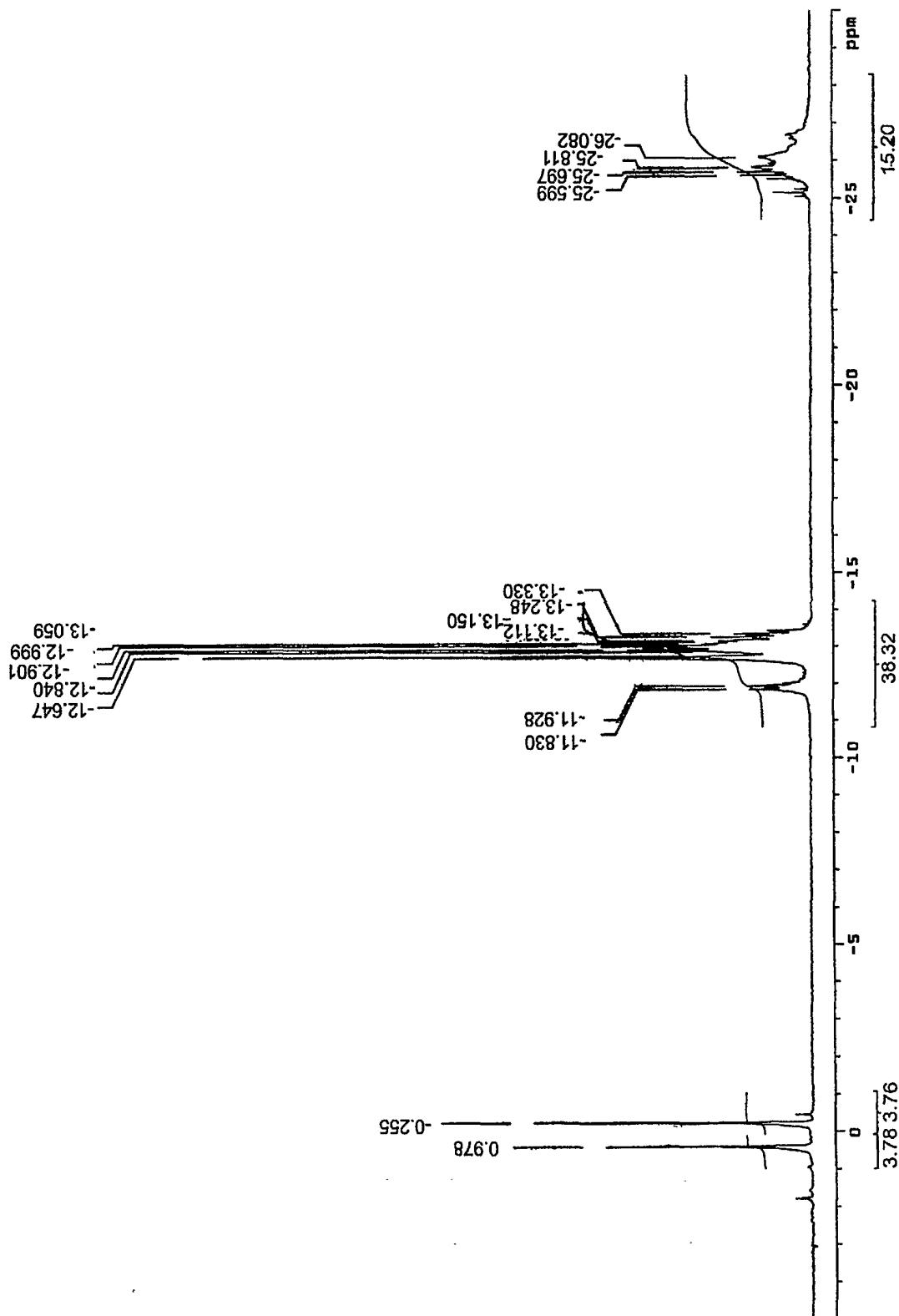


Fig. 15a

10/14

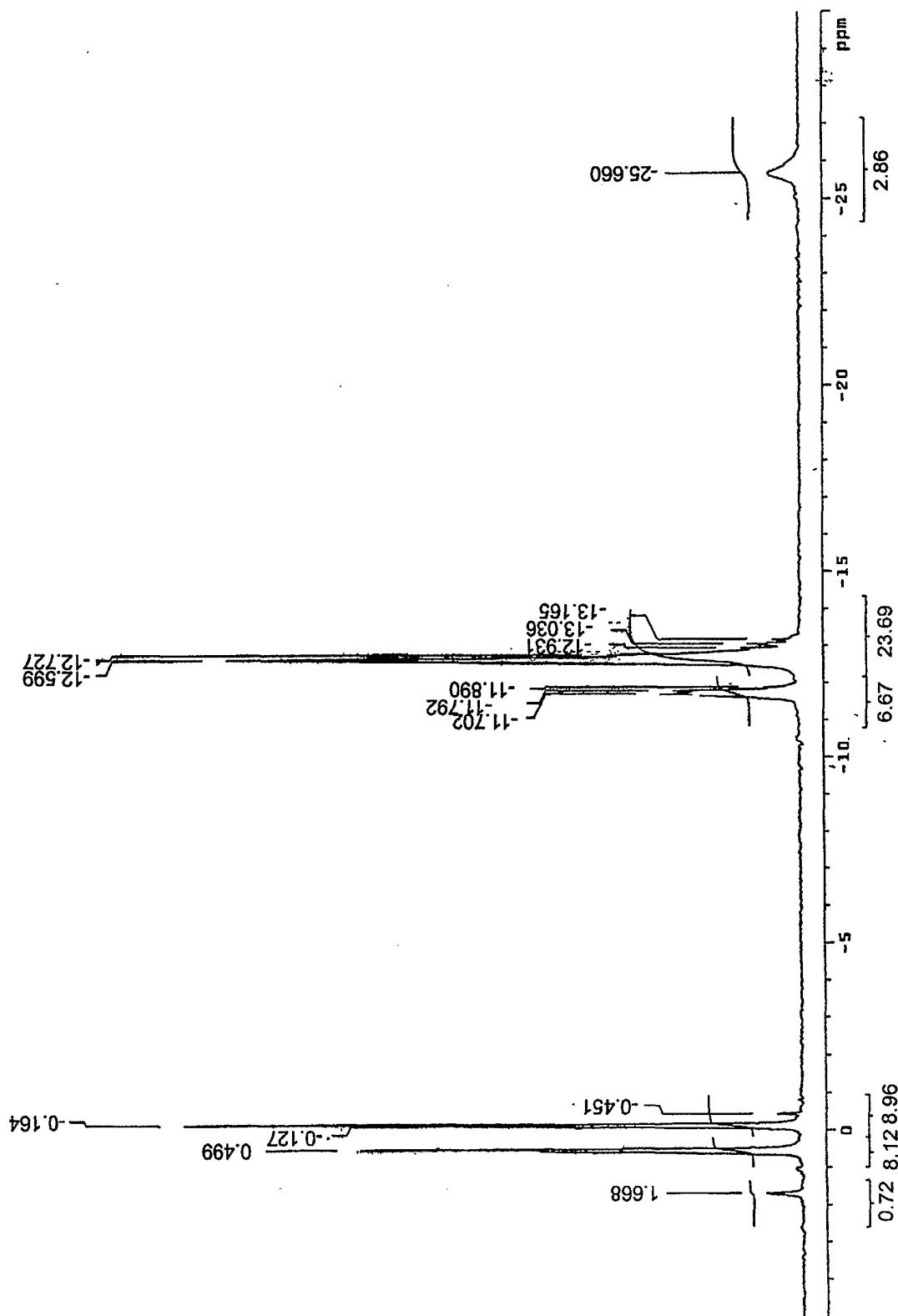


Fig. 15b

11/14

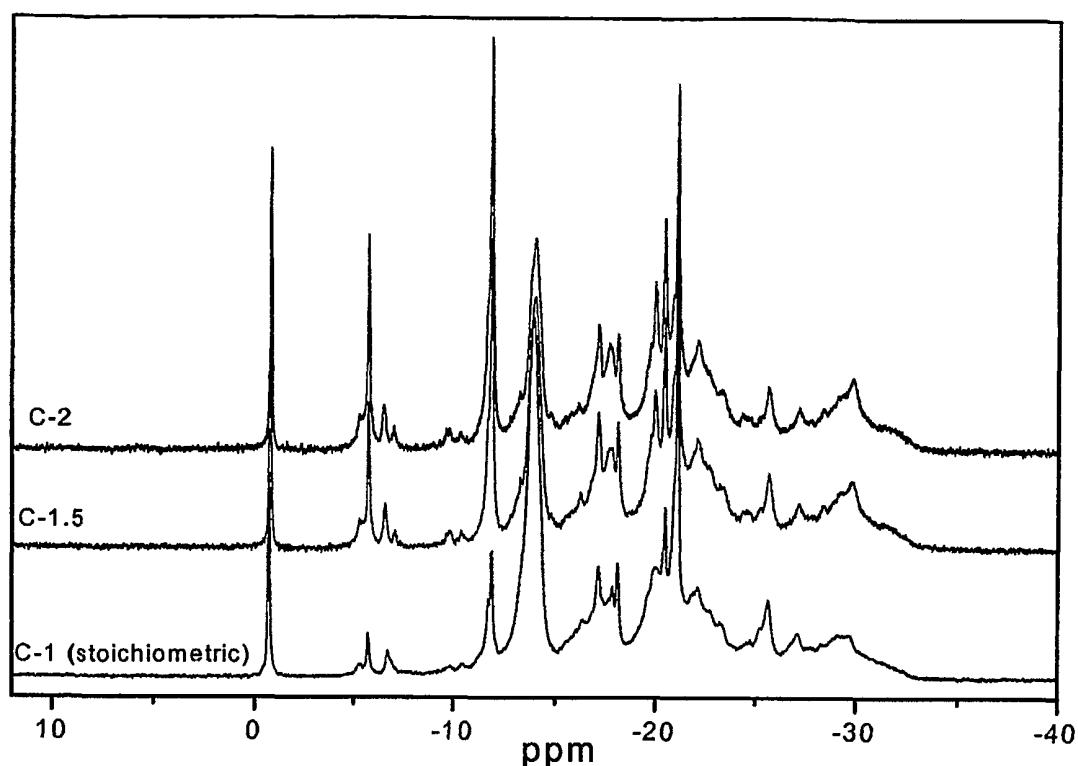


Fig. 16a

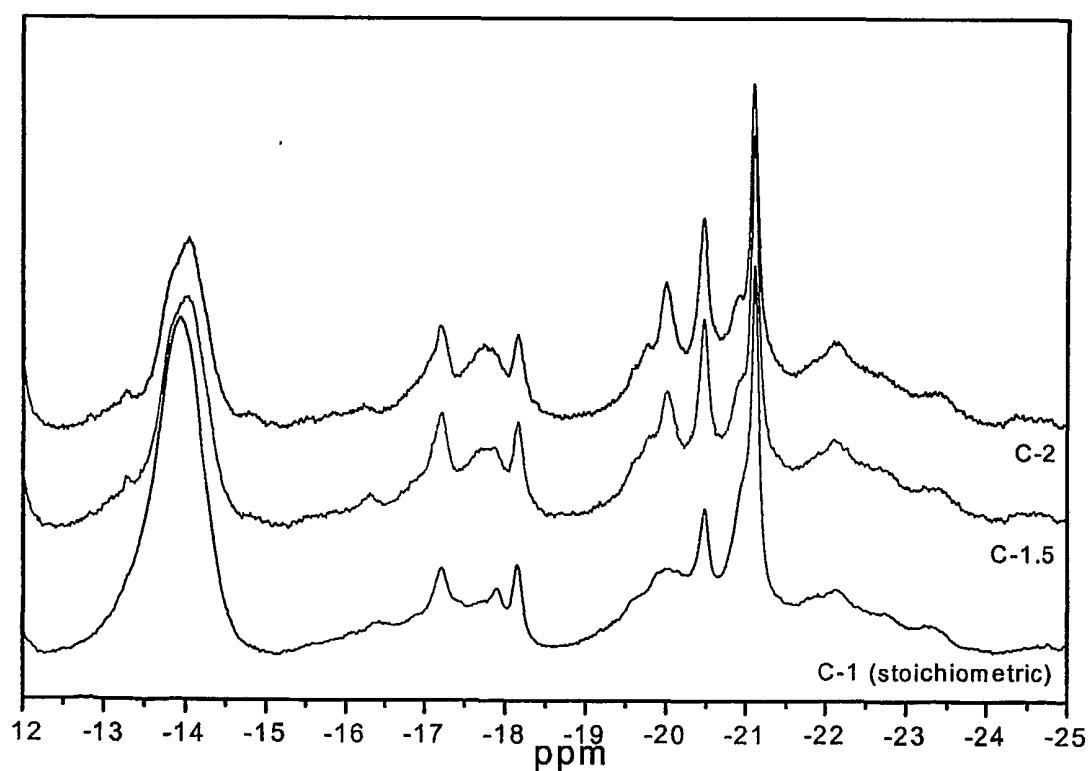


Fig. 16b

12/14

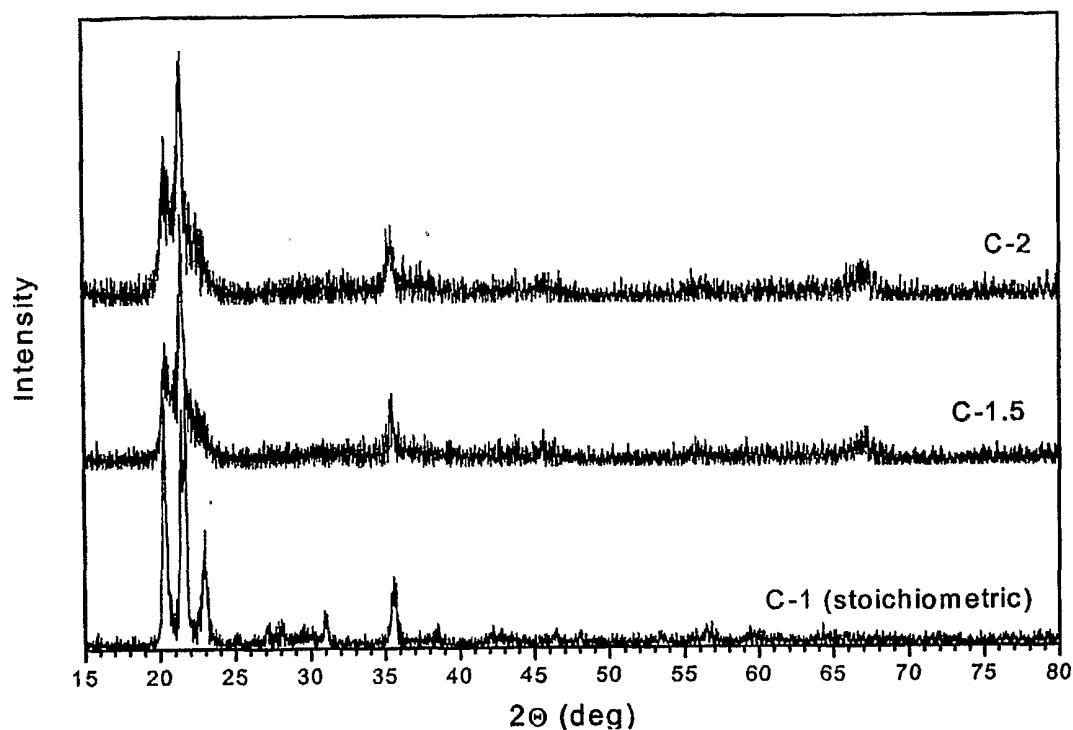


Fig. 17a

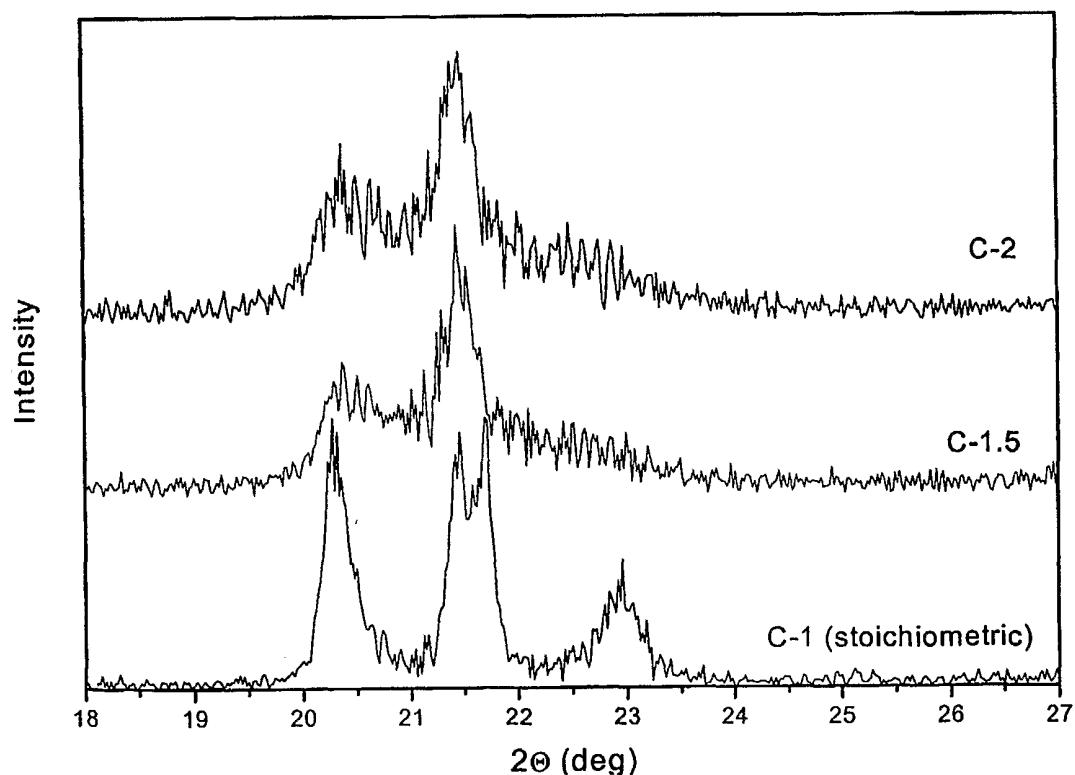


Fig. 17b

13/14

Fig. 18

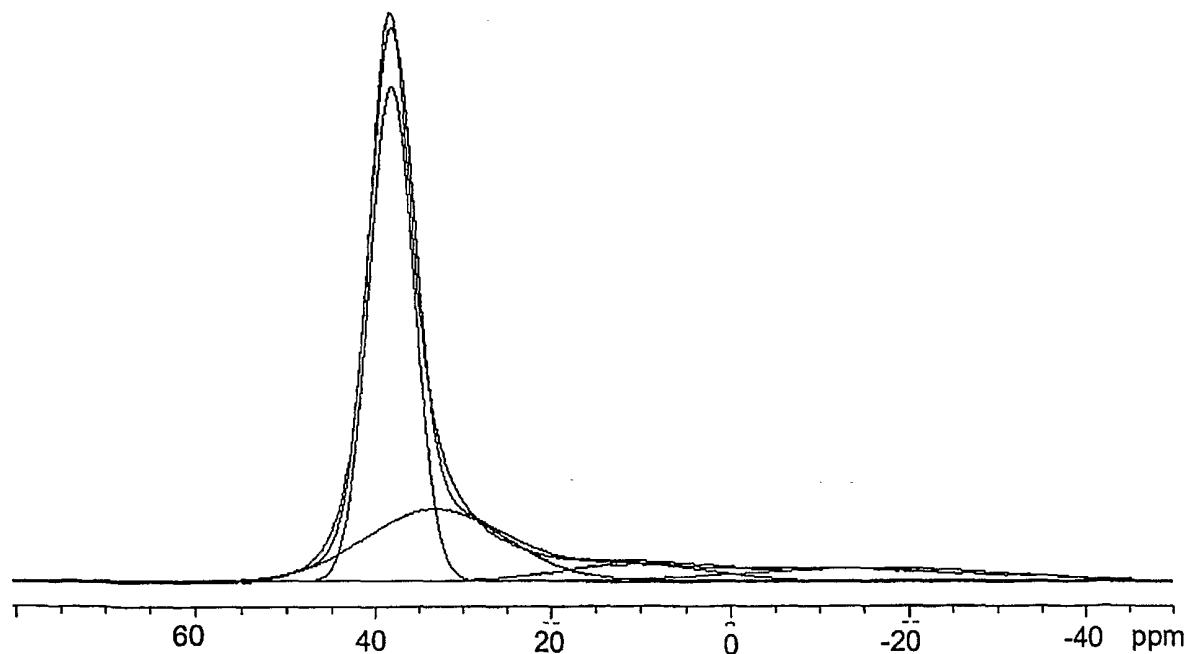
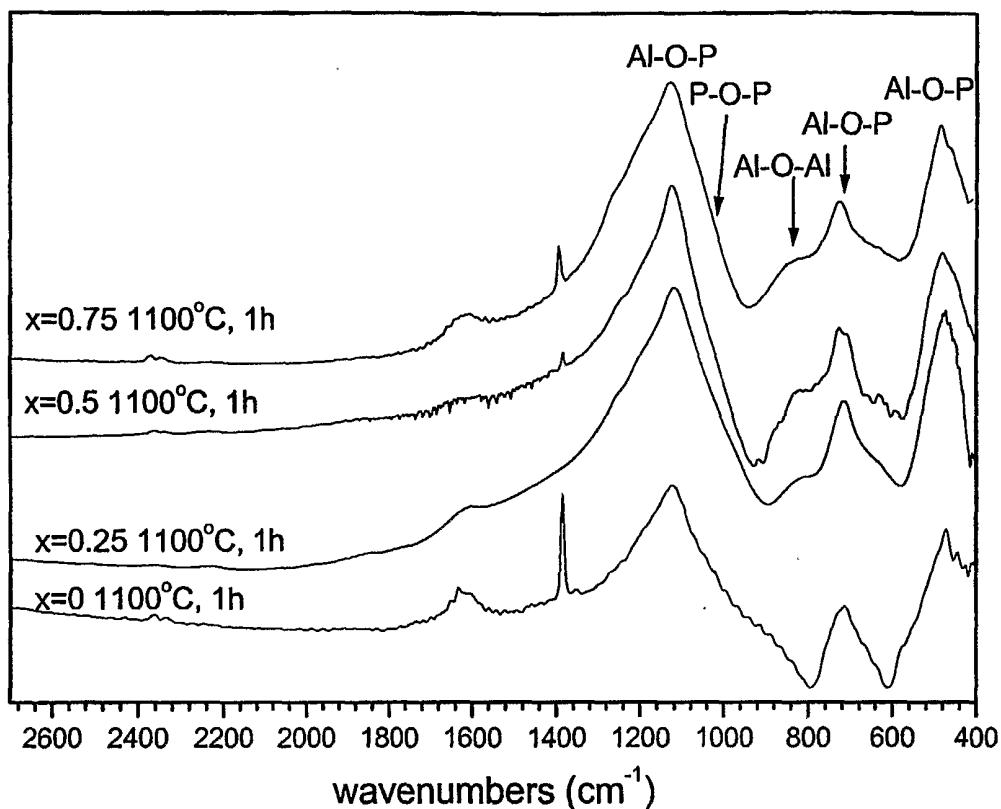
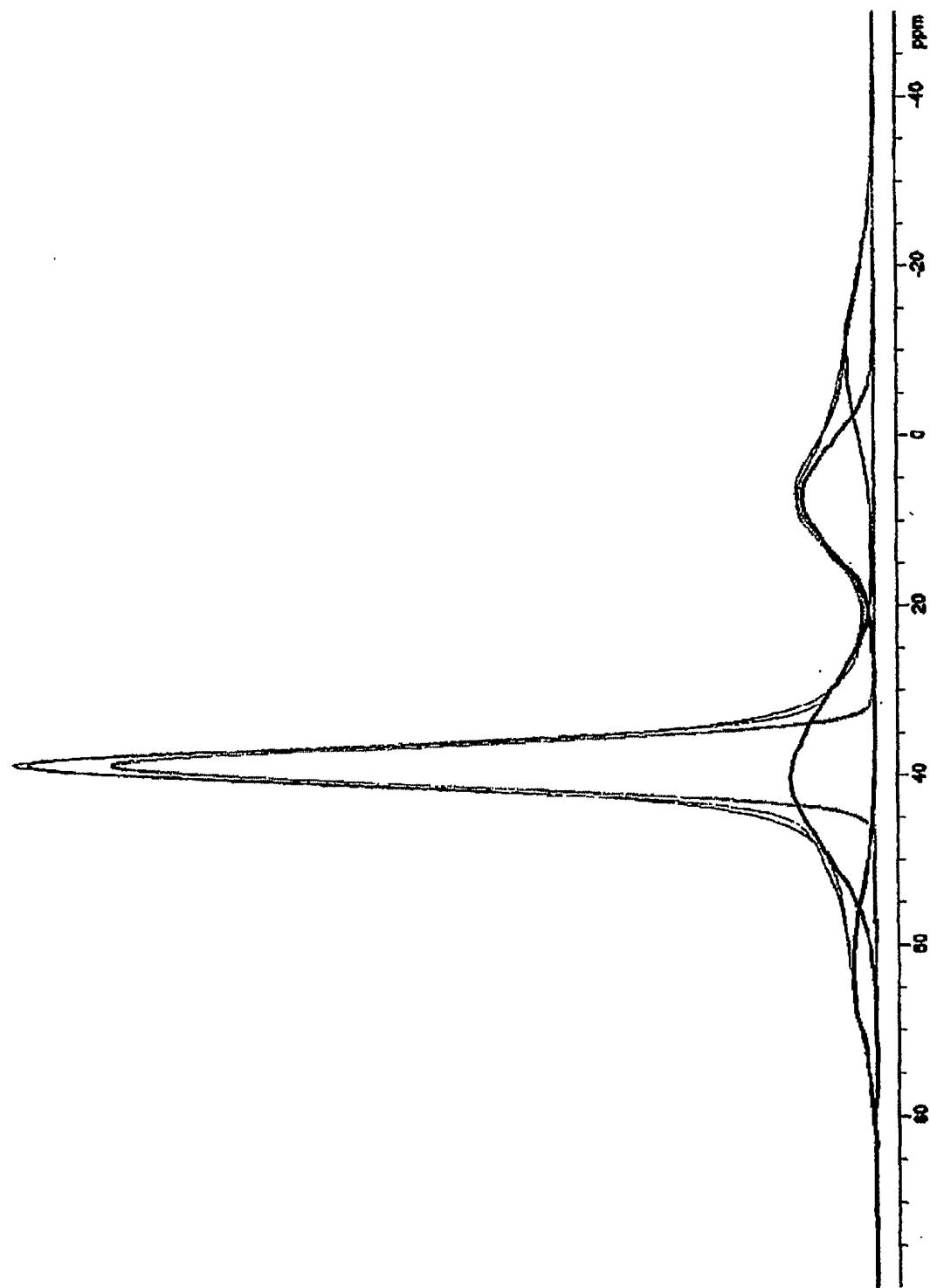


Fig. 19

Fig. 20

14/14



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/41790

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C01B 25/36; C01F 7/00

US CL :106/14.05, 14.21; 252/387, 397; 428/305

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/14.05, 14.21; 252/387, 397; 428/305

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,289,863 A (HILL et al) 15 September 1981, abstract and claims.	1,6,7
X	US 5,698,758 A (RIESER et al) 16 December 1997, abstract and claims.	1,6,7
X	US 6,022,513 A (PECORARO et al.) 08 February 2000, abstract, col. 4, lines 23+ and claims.	1,7
Y	US 4,551,652 A (COMPEN et al.) 05 November 1985, abstract, examples and claims.	16-22
Y	GB 1396795 A (FERRIE et al.) 04 June 1975, entire document.	16-22
Y	GB 1451145 A (MATSUMISHIMA et al.) 29 September 1976, examples and claims.	16-22

Further documents are listed in the continuation of Box C.

See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

11 DECEMBER 2001

Date of mailing of the international search report

11 JAN 2002

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231Authorized officer  
  
ANTHONY J. GREEN

Facsimile No. (703) 305-3290

Telephone No. (703) 308-0661

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US01/41790

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:  
1-7 and 9-22
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

The additional search fees were accompanied by the applicant's protest.



No protest accompanied the payment of additional search fees.

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US01/41790

**BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING**

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 18.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1-7, drawn to an aluminum phosphate composition possessing a ratio of aluminum to phosphorus of greater than one-to-one.

Group II, claim 8, drawn to a method of protecting a substrate from corrosion using a precursor solution.

Group III, claims 9-22, drawn to a metastable material comprising an aluminum phosphate composition having the formula  $Al_{1+x}PO_{4+3x/2}$  wherein x is about 0 to about 1.5.

Group IV, claims 23-26, drawn to a method of using aluminum content of an aluminum phosphate compound to affect the metastability of said material.

Group V, claims 27-31, drawn to an aluminum phosphate product having Al-O-Al structural moieties.

The inventions listed as Groups I-V do not relate to a single inventive concept under PCT Rule 18.1 because, under PCT Rule 18.2, they lack the same or corresponding special technical features for the following reasons:

Groups II-V do not require the particulars of Group I, namely an aluminum phosphate composition having a ratio of aluminum to phosphorus of greater than one-to-one. Note that Groups II and IV use materials other than those of Group I and that Groups III and V are products possessing limitations other than those recited in Group I.