



Oficina de
Propiedad
Intelectual

Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

Copia Oficial Certificada

Yo, el suscrito, quien soy un funcionario debidamente autorizado de conformidad con los numerales (1) y (4) del artículo 74 de la Ley de Desregulación y Contratación Externa de 1994 para la firma y expedición de certificados a nombre del Contralor General, por el presente certifico que se adjunta al presente una copia fiel de los documentos, tal como fueron inicialmente presentados en relación con la solicitud de patente GB1820094.9, presentada el 10 de diciembre de 2018 y tal como se encuentra almacenada en forma electrónica en el Sistema de Expedientes Electrónicos de Patentes.

El Sistema de Expedientes Electrónicos de Patentes cumple la Norma Británica BS10008- Fuerza probatoria y admisibilidad jurídica de información almacenada electrónicamente y la norma ISO15801- Imaginería Electrónica - información almacenada electrónicamente, recomendaciones para veracidad y confiabilidad.

De conformidad con las Reglas de Patentes (Nuevo Registro de Compañías) de 1982, si una compañía mencionada en este

DIEGO F. VARGAS Z
TRADUCTOR E INTÉRPRETE OFICIAL
ESPAÑOL - INGLÉS - INGLÉS - ESPAÑOL
RES. 0001 DE ENERO 4 DE 1999
MINISTERIO DE JUSTICIA

certificado y en cualquier documento acompañante, se ha vuelto a registrar de conformidad con la Ley de Compañías de 1980, con el mismo nombre con el cual se había registrado inmediatamente antes del nuevo registro, salvo por la sustitución o inclusión en la última parte de su nombre de los vocablos "compañía pública limitada" o sus equivalentes en galés, las referencias en el presente certificado al nombre de la compañía y a cualquier documento acompañante serán tratadas como referencias al nombre con el cual esta se volvió a registrar.

De conformidad con las reglas, las palabras "compañía pública limitada" podrán ser reemplazadas por p.l.c., plc, P.L.C. o PLC.

El nuevo registro de conformidad con la Ley de Compañía no constituye una nueva persona jurídica sino que simplemente somete a la compañía a ciertas normas jurídicas adicionales sobre compañías.

Firmado *Firma Ilegible*

Fechado 31 de enero de 2019

FIN DE LA TRADUCCIÓN

Bogotá D.C., 27 de febrero de 2019

Es traducción fiel y completa del documento original realizada por: DIEGO F. VARGAS ZAMORA,
Traductor e Intérprete Oficial, Resolución No. 0001 de 1999 del Ministerio de Justicia de Colombia.

DIEGO F. VARGAS Z.
TRADUCTOR E INTERPRETE OFICIAL
ESPAÑOL - INGLÉS - INGLÉS - ESPAÑOL
RES. 0001 DE ENERO 4 DE 1999
MINISTERIO DE JUSTICIA



Intellectual
Property
Office

Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

Certified Office Copy

I, the undersigned, being an officer duly authorised in accordance with section 74(1) and (4) of the Deregulation & Contracting Out Act 1994 to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with patent application GB1820094.9 filed on 10 December 2018, and as stored electronically on the Patents Electronic Case file System.

The Patents Electronic Case-file System is compliant with British Standard BS10008 - Evidential weight and legal admissibility of information stored electronically and ISO15801 - Electronic imaging - information stored electronically, recommendations for trustworthiness and reliability.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Dated 31 January 2019



Intellectual
Property
Office

1200310836
1018032381 D10225
10/12/2018 650.00 DepositAccount

Patents Form 1
Patents Act 1977 (Rule 12)

Request for grant of a patent

Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

Application number GB 1820094.9

1. Your reference	K23-1531-06GB		
2. Full name, address and postcode of the applicant or of each applicant	Kastus Technologies DAC Temple Chambers 3 Burlington Road Dublin 4 D04 RD68 Ireland		12381083001
Patents ADP number (if you know it)			
3. Title of the invention	P-doped surface coatings and process of preparation thereof		
4. Name of your agent (if you have one) "Address for service" to which all correspondence should be sent. This may be in the European Economic area or Channel Islands (see warning note below) (including the postcode) Patents ADP number (if you know it)	Hanna, Moore + Curley Hanna, Moore + Curley Garryard House 25/26 Earlsfort Terrace Dublin D02 PX51 Ireland		09931734001
5. Priority declaration: Are you claiming priority from one or more earlier-filed patent applications? If so, please give details of the application(s)			
Country	Application number	Date of filing	PDAS Access Code
6. Divisionals etc: Is this application a divisional application, or being made following resolution of an entitlement dispute about an earlier application. If so, please give the application number and filing date of the earlier application	Number of earlier UK application	Date of filing (day / month / year)	
7. Inventorship: (Inventors must be individuals not companies)			
Are all the applicants named above also inventors?	No		
8. Are you paying the application fee with this form?	Yes		

(REV DEC07)

Intellectual Property Office is an operating name of the Patent Office

Patents Form 1(e)
<https://www.gov.uk/ipo>

Patents Form 1

9. Accompanying documents: please enter the number of pages of each item accompanying this form.

Continuation sheets of this form

Description: 23

Claim(s): 5

Abstract: 1

Drawing(s): 19

If you are not filing a description, please give details of the previous application you are going to rely upon

Country	Application number	Date of filing	PDAS Access Code
---------	--------------------	----------------	------------------

10. If you are also filing any of the following, state how many against each item.

Priority documents: 0

Statement of inventorship and right to grant of a patent
(Patents Form 7): 1

Request for search (Patents Form 9A): 1

Request for a substantive examination (Patents Form 10): 1

Any other documents (please specify): PDAS Registration Form
Covering Letter

11. I/We request the grant of a patent on the basis of this application.

Signature: Subject: Marie Walsh 16153; Issuer:
European Patent Office, European Patent
Office CA G2

Date: 10 Dec 2018

12. Name, e-mail address, telephone, fax and/or mobile number, if any, of a contact point for the applicant

WALSH, Marie
Email: docket@hmc-ip.com
Telephone: +353 1 661 3930
Fax: +353 1 661 3453

Warning

After an application for a patent has been filed, the Comptroller will consider whether publication or communication of the invention should be prohibited or restricted under section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you are resident in the United Kingdom and your application contains information which relates to military technology, or would be prejudicial to national security or the safety of the public, section 23 of the Patents Act 1977 prohibits you from applying for a patent abroad without first getting written permission from the Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked. Until such time or until the revocation of any direction, for any such application the address for service referred to at part 4 above must be in the United Kingdom.

Although you may have an address for service in the Channel Islands, any agent instructed to act for you must reside or have a place of business in the European Economic Area or Isle of Man.

Title

P-doped surface coatings and process of preparation thereof

Field

- 5 The present application relates to anti-microbial coatings for surfaces; and more particularly to coatings doped by phosphorus which are referred to as "P-doped coatings" and which are active in both the UV and visible light spectrum.

Background of The Invention

- 10 TiO₂ has been extensively used in different photocatalytic applications including antimicrobial coatings. The main photoactive polymorphs of TiO₂ are anatase and brookite, with anatase being the most efficient. The photocatalytic effect initiates by absorbing light with an energy equal to or greater than the bandgap of TiO₂. Consequently, the electrons in the valence are excited to the
15 conduction band, while positive holes form in the valence band. These photoexcited electrons and photogenerated positive holes are responsible for photocatalytic reactions.

- To make photocatalysts responsive to visible light, it is necessary to narrow the band gap energy between the valence band and the conduction
20 band or to form other energy levels between them. Nevertheless, the bandgap of TiO₂ (anatase phase ≈ 3.2 to 3.3 eV) lies in the UV region of the electromagnetic spectrum, limiting its photoactivation under visible light. This has become the driving force for developing various strategies in an effort to modify the bandgap of TiO₂.

- 25 Tuning the electrical properties of TiO₂ can be performed in different ways; and doping (including doping by metal or non-metal, or co-doping) is one of the effective approaches to fulfil this objective. Non-metal doping is one of the methods to shift the photoactivation of anatase TiO₂ into the visible range. This group of dopants has two sub-groups namely cationic and anionic, with anions
30 narrowing the bandgap and cations injecting electrons into the conduction band and creating intermediate energy levels.

Phosphorus as a dopant allows the possibility of both cationic (P^{5+}) and anionic (P^{3-}) doping of anatase TiO_2 . In the pentavalent state (P^{5+}), phosphorus can induce a blue-shift and an increase in the free charge carriers of phosphorus-doped TiO_2 films.

5 International patent application no. WO2015/091261 discloses a process for the preparation of a photocatalytically active antimicrobial surface coating. The process mixes a chelating agent with titanium alkoxide and fluoroacetic acid, and subsequently adds an aqueous solution to the mixture.

Fluoroacetic acid is a highly corrosive acid and therefore it is
10 advantageous to replace it with a less corrosive, more user-friendly acid. The application presents the development of a P-doped titania antimicrobial coating solution which has several advantages over the existing technology.

The advantages of the present invention result from the elimination of TFA and the inclusion of a phosphoric acid or derivative thereof, which in turn leads
15 to improved process-related aspects: decreasing production cost, increasing the efficiency of doping, or reducing the acidity due to phosphoric acid being less corrosive than TFA, and, due to the non-volatility of phosphoric acid, the possibility of its addition at a later stage in the synthesis, thus resulting in the composition and doping level being customisable from a standard stock sol.
20 Surprisingly, in addition, the anatase phase is present at higher temperatures when using the novel technology than when using F-doping.

Summary

Accordingly, the present invention provides a process for the preparation
25 of an antimicrobial coating solution, the process comprising the steps of:

- (i) Mixing a chelating agent with a titanium alkoxide and a phosphorylating agent; and
- (ii) Adding an aqueous solution to the mixture formed from step (i).

The present invention also provides a process according to the above process, wherein the aqueous solution is added in step (i) and the phosphorylating agent is added in step (ii).

5 The present invention also provides a process according to the above process, wherein the aqueous solution and the phosphorylating agent are added in step (ii).

10 The present invention also provides a process for making an antimicrobial powder comprising the initial step of preparing a solution in accordance with any preceding claim, evaporating the solvents from the solution and then annealing the residue at a temperature between 300 °C and 1400 °C.

15 The present invention also provides a method of preparing an antimicrobial coating composition comprising the step of mixing an antimicrobial powder as prepared by the process of claim 23 with a coating solution as prepared by the above processes.

20 The present invention also provides an antimicrobial coating composition obtained by the above method, wherein the coating composition is UV and visible light activated.

25 The present invention also provides an antimicrobial coating composition obtained by the above method, wherein the coating composition exhibits antimicrobial activity under both UV and visible light and in reduced light. The present invention also provides an antimicrobial coating composition obtained by the above method, wherein the coating composition is stable at temperatures up to 1400 °C.

30 The present invention also provides an antimicrobial coating composition comprising a hydrolysed phosphorus-sol.

The present invention also provides an antimicrobial coating composition comprising a transparent phosphorus-doped titania coating.

- 5 The present invention also provides an antimicrobial coating composition comprising phosphorus-doped titanyl acetate.

The present invention also provides a method for coating a substrate, the method comprising the steps of

- 10 (i) Depositing an antimicrobial coating solution prepared according to the process described above or an antimicrobial coating composition as described above, on a substrate
(ii) Drying said coating; and
(iii) Exposing the coated substrate to a temperature above 300 °C for a
15 period of time in the range of 20 minutes to 30 hours.

The present invention also provides a coated substrate comprising an antimicrobial coating prepared by the process as described above.

- 20 One of the main advantages of P-doped coating solutions lies in the final production cost which in turn affects the marketed price for customers.

- The P precursor used during solution production is non-volatile and non-oxidising. This makes the handling, storage and application of the solution
25 straightforward. Moreover, no additional extraction and filtering system is needed on the production line.

Phosphoric acid is stable, even under thermal exposure conditions.

- 30 The anatase phase is present in the system to a large extent even at temperatures as high as 1100°C. This increases the product's potential

applications, with many manufacturers requiring firing conditions at this temperature and above.

A first embodiment of the application provides a process for the
5 preparation of an antimicrobial coating solution using orthophosphoric acid.

In one aspect, the present teaching provides a process for the preparation of an antimicrobial coating solution, the process comprising the steps of:

- (i) mixing a chelating agent with titanium alkoxide and orthophosphoric acid;
and
- 10 (ii) adding an aqueous solution to the mixture from step (i).

It is to be understood that in the preferred embodiment, the aqueous solution comprises solely water as the solvent. However, in an alternative embodiment, the aqueous solution can also comprise organic solvents such as
15 alcohols including, but not limited to, ethanol, methanol or isopropanol, in an amount up to 80 water: 20 organic solvent. However, this inclusion of an organic solvent would increase the 'carbon foot print' and the cost would be higher than in the embodiments in which the aqueous solution relies entirely on water as the solvent.

20

An advantage of the process according to the present teaching is that it allows for a thin homogeneous coating to be applied to a substrate (in this context, the term "thin" means approx 20nm to 200nm thickness for a single or multiple layer(s) and still provide for effective antimicrobial action, the end
25 product being transparent to the user.

The addition of an aqueous solution is counter intuitive because normally the addition of water would cause the titanium dioxide to precipitate out. However, it has been found that by using a high ratio of the aqueous solution to
30 the other components that precipitation is avoided. The term, "high ratio" means above 50 moles times (e.g. for every 1 mole of titania precursor 50 or more

mole times aqueous solution is required). Ideally, between 90 to 200 mole times is used to ensure full dissolution). (Any solvent ratio lower than 50 mole times would not achieve the advantageous results of the present invention).

- 5 In this specification, weight % (wt%) is to be construed as meaning weight % relative to the weight of the total composition.

The chelating agent may be a carboxylic acid.

- 10 The carboxylic acid may be selected from the group consisting of formic acid, propionic acid, butanoic acid and acetic acid.

- Preferably, the carboxylic acid is acetic acid. The preferred form of acetic acid is glacial acetic acid. Where the acetic acid is selected as the chelating agent, the preferred form is glacial acetic acid to prevent reaction between water and the titanium alkoxide prior to the step of adding the aqueous solution. The amount of glacial acetic acid used may be in the range 1 to 40 wt%; preferably in the range 1 to 20%; and most preferably, in the range 2 to 10 wt%; and with the range 12 to 18 wt% being optionalimal.
- 15

- 20 The titanium alkoxide may be selected from the group consisting of titanium isopropoxide, titanium ethoxide, titanium methoxide and titanium butoxide. The preferred titanium alkoxide is titanium isopropoxide as its performance has been clearly demonstrated to provide an effective coating solution.

- 25 The amount of titanium isopropoxide used may be in the range 4 to 15 wt %, preferably 6 to 12 wt%.

- The phosphoric acid is preferably orthophosphoric acid. Other phosphorylating agents may be selected from the group consisting of phosphorus pentoxide, ammonium dihydrogen phosphate and diammonium hydrogen phosphate.
- 30

The amount of orthophosphoric acid used may be in the range 0.0001 to 1 %, preferably in the range 0.0002 to 0.005%.

5 The amount of water used may be in the range 30 to 99.5 wt%, preferably 40 to 99 wt%; and most preferably, 50 to 95 wt%. (Wt% water compared to the wt of the total composition).

The process may be carried out at a temperature between 10 and 65 °C.

10 In one aspect, the present teaching provides a process for making an antimicrobial powder, the process comprising the initial step of preparing a solution in accordance with the process described herein and then evaporating the solvents and then annealing the residue at a temperature between 300 °C and 1400 °C.

15 In a further aspect, a method of preparing an antimicrobial coating is provided, the method comprising the step of mixing an antimicrobial powder as prepared by the process described herein, with a coating composition.

20 Preferably, the coating composition comprises an aqueous solution and the method comprises the step of phosphorylating the solution with a phosphorylating agent. The phosphorylating agent may be selected from a range including orthophosphoric acid, phosphorus pentoxide, ammonium dihydrogen phosphate and diammonium hydrogen phosphate including said
25 derivatives.

A visible light activated antimicrobial coating composition is obtained by the method described herein. The coating described herein can be used under indoor lighting conditions. The antimicrobial coating composition exhibits
30 antimicrobial activity under visible light and in reduced light.

The antimicrobial compositions described herein are stable at high temperatures. Suitably, the antimicrobial coatings composition described herein is stable at temperatures up to at 1400°C.

- 5 A method for coating a substrate is provided, the method comprising the steps of
- (i) depositing an antimicrobial coating solution prepared according to the process described herein or an antimicrobial coating composition described herein, on a substrate;
 - 10 (ii) drying said coating; and
- exposing the coated substrate to a temperature above 300°C for a period of time in the range 20 minutes to 30 hours.

The coated substrate may be exposed to a temperature in the range
15 300°C to 1400°C. Where the substrate is glass or comparable composite material, the temperature is preferably in the range of 350°C to 700°C, most preferably 450°C to 590°C.

In the case where the substrate is a ceramic material, the third step (iii)
20 may be a firing process. The temperature may be between 350-800°C for a second firing step or the temperature may be between 500-1400°C for a firing process having a single firing.

Suitably, the composition according to the present teaching can be applied
25 in liquid form to a substrate to provide a coating.

The liquid coating may be deposited by any suitable method. Suitable methods may include but are not limited to spraying, dipping, roller, brush, electrostatic and spin-coating.

30 Suitably, the present application provides an antimicrobial coating composition comprising phosphorus-doped titanyl acetate. Advantageously, this may be in

the form of a gel or a compressed tablet which may be packaged and shipped to locations where the coating composition is to be applied. The advantage being that the coating composition may be manufactured and packaged for shipping in relatively small amounts reducing packaging and shipping costs. A further
5 advantage is that the shelf life is effectively lengthened by at least several months. At the location of the coating process, water may be added as required. Once the water is added the phosphorus-doped titanyl acetate is hydrolysed.

In a further aspect, the present teaching provides a coated substrate comprising
10 an antimicrobial coating prepared by the process described herein or an antimicrobial coating composition described herein.

The substrate may be selected from the group consisting of glass and related composite materials, ceramics, plastic, cement and clay. Where the substrate is
15 glass, the glass may be, for example, a chemically strengthened glass or tempered glass. In specific applications, the substrate may be a clay brick, ceramic tile or element of sanitary ware.

Brief Description Of The Drawings

20 The present application will now be described with reference to the accompanying drawings in which:

Figure 1 is a schematic of photocatalytic activity of a TiO_2 surface;

Figure 2 is a Raman spectrum of KCS 110 @ 900°C;

Figure 3 is a Raman spectrum of KCS 110 @ 950°C;

25 Figure 4 is a Raman line-scan spectrum of KCS 110 @ 1000°C;

Figure 5 is a Raman imaging of KCS 110 @ 1000°C;

Figure 6 is a Raman spectrum of KCS 111 @ 700°C;

Figure 7 is a Raman spectrum of KCS 111 @ 900°C;

Figure 8 is a Raman spectrum of KCS 111 @ 950°C;

30 Figure 9 is a Raman spectrum via line-scan mode from KCS111 @ 1000°C;

- Figure 10 is an Optical micrograph (left) and Raman imaging maps of anatase and rutile phases from the scanned red square area (right) of KCS 111 @ 1000 °C;
- Figure 11 is a total average spectrum and anatase and rutile maps of KCS 111 @ 1100°C;
- Figure 12 is a Raman spectrum of KCS 112 @ 900°C;
- Figure 13 is a Raman spectrum of KCS 112 @ 950°C;
- Figure 14 is an optical micrograph, total average spectrum, and anatase, rutile, TPP phase Raman maps from KCS112 @ 1000°C;
- Figure 15 is an optical micrograph, total average spectrum, and various phases Raman maps of KCS 112 @ 1100 °C;
- Figure 16 is an XRD spectrum of KCS 110 @700°C;
- Figure 17 is an XRD spectrum of KCS 100 @ 900°C;
- Figure 18 is an XRD spectrum of KCS 110 @ 950°C;
- Figure 19 is an XRD spectrum of KCS 110 @ 1000°C;
- Figure 20 is an XRD spectrum of KCS 110 @ 1100°C;
- Figure 21 is an XRD spectrum of KCS 111 @ 700°C;
- Figure 22 is an XRD spectrum of KCS 111 @ 900°C;
- Figure 23 is an XRD spectrum of KCS 111 @ 950°C;
- Figure 24 is an XRD spectrum of KCS 111 @ 1000°C;
- Figure 25 is an XRD spectrum of KCS 111 @ 1100°C;
- Figure 26 is an XRD spectrum of KCS 112 @ 700°C;
- Figure 27 is an XRD spectrum of KCS 112 @ 900°C;
- Figure 28 is an XRD spectrum of KCS 112 @ 950°C;
- Figure 29 is an XRD spectrum of KCS 112 @ 1000°C;
- Figure 30 is an XRD spectrum of KCS 112 @ 1100°C;
- Figure 31 is a UV spectrum of KCS 110 @ 700°C;
- Figure 32 is a UV spectrum of KCS 110 @ 900°C;
- Figure 33 is a UV spectrum of KCS 111 @ 700°C;
- Figure 34 is a UV spectrum of KCS 111 @ 900°C;
- Figure 35 is a UV spectrum of KCS 112 @ 700°C;

- Figure 36 is a UV spectrum of KCS 112 @ 900°C;
 Figure 37 is a UV spectrum of KCS 112 @ 900°C – extrapolated intercept of the
 V absorption range into the visible range;
 Figure 38 is a UV spectrum of KCS 117 @ 700°C; and
 5 Figure 39 is a UV spectrum KCS 118 @ 700°C.

Detailed Description Of The Drawings

- The present application provides an industrially viable water-based
 environmentally benign, processing technology for the production of
 10 antimicrobial coating solutions.

- The P-doped anti-microbial coating solution described herein is eco-
 friendly which is highly desirable. The solution used is water based and the
 phosphorus doping agent is more environmentally favourable in comparison to
 15 it's corrosive trifluoroacetic acid counterpart.

- Orthophosphoric acid was chosen as the preferred phosphorus source as
 it is readily available in high purity, is non-toxic, non-volatile, relatively
 inexpensive and as an acid, does not introduce any cations not already present
 20 in the sol. in the phosphorus source, such as orthophosphoric acid, is suitable
 for use in the process and can be used in relatively low concentrations (in the
 range of 0.0001 to 1 wt%), since losses through evaporation prior to firing will
 be minimal.

- 25 The present invention will now be described with reference to the following
 examples which are provided, by way of example only.

P-Doping amounts

Batch	Volume GPA added (ml)	(x doping)	GPA % v/v
KCS110	0.057	1	0.0004
KCS111	0.14	2.46	0.0009

KCS112	0.5	8.77	0.0033
KCS117	0.14	2.46	0.0009
KCS118	0.14	2.46	0.0009

Table 1. P-Doping amounts

The formulation may optionally include a dispersing agent, to increase the stability of the titanium dioxide dispersion, over and above that achieved by the ionic double layer repulsion resulting from adsorption of the dissociated acids. Such a dispersing agent should ideally be added to the formulation after the hydrolysis is complete. Suitable dispersing agents include organic compounds such as alkanes and alkene oligomers modified with multiple carboxylic acid groups, amine groups or alcohols on side chains. Examples of suitable dispersing agents include Disperbyk 180, Disperbyk 2060, Disperbyk 2061, Disperbyk 2062, Disperbyk 2080, Disperbyk 2081 and Disperbyk 2205. The five samples, logged as KCS110, KCS111,KCS112, KCS 117 and KCS 118 were prepared as follows.

Example 1

Examples 1 – 3 describe an embodiment of the invention wherein the order of addition is as follows:

- a) tetraisopropoxide
- b) glacial acetic acid
- c) orthophosphoric acid (aqueous) and finally
- d) de-ionised water.

In an alternative embodiment a dispersing agent may be added following the addition of de-ionised water.

KCS110:

1. 10mL titanium tetraisopropoxide (TTIP) was placed in a polypropylene beaker.

- 5
2. 19.2mL glacial acetic acid was added while stirring.
 3. 0.057mL 86% orthophosphoric acid (aqueous) was added while stirring.
 4. 120mL deionised water was added while stirring and the mixture stirred for a further 40 minutes, to form a colourless, slightly hazy sol, which was then bottled.

Example 2

KCS111:

- 10
1. 10mL TTIP was placed in a polypropylene beaker.
 2. 19.2mL glacial acetic acid was added while stirring.
 3. 0.14mL 86% orthophosphoric acid (aqueous) was added while stirring. A small quantity of white precipitate began to form.
 4. 120mL deionised water was added while stirring and the mixture stirred for a further 40 minutes. A sol with a translucent milky white appearance was formed and the precipitate previously formed re-dispersed, which was then bottled.
- 15

Example 3

20 KCS112:

1. 10mL TTIP was placed in a polypropylene beaker.
 2. 19.2mL glacial acetic acid was added while stirring.
 3. 0.5mL 86% orthophosphoric acid (aqueous) was added while stirring. A larger quantity of white precipitate began to form than in the case of KCS111.
 4. 120mL deionised water was added while stirring and the mixture stirred for a further 40 minutes. A sol with a translucent milky white appearance was formed, that was denser in colour than KCS111, which was then bottled.
- 25
- 30

Example 4

Example 4 describes an alternative embodiment, wherein the order of addition of the reagents is as follows:

- 35
- a) TTIP
 - b) Glacial acetic acid
 - c) De-ionised water
 - d) Orthophosphoric acid (aqueous)

A dispersing agent may be added following the addition of orthophosphoric acid.

5 **KCSI 17:**

Orthophosphoric acid can be added after the addition of the deionised water to the glacial acetic acid/TTIP mixture.

1. 10mL TTIP was placed in a polypropylene beaker.
- 10 2. 19.2mL glacial acetic acid was added while stirring.
3. 120mL deionised water was added while stirring and the mixture stirred for 20 minutes. A sol with a translucent milky white appearance was formed.
4. 0.14mL 86% orthophosphoric acid (aqueous) was added while stirring. A small quantity of white precipitate began to form. The sol was stirred for a
- 15 further 40 minutes and this precipitate re-dispersed.

Example 5

20 Example 5 describes an alternative embodiment, wherein the order of addition of the reagents is as follows:

- a) TTIP
- b) Glacial acetic acid
- c) Orthophosphoric acid (aqueous) dissolved in de-ionised water

25 A dispersing agent may be added following the addition of orthophosphoric acid.

KCSI 18:

30 Orthophosphoric acid can be added at the same time as the addition of the deionised water to the glacial acetic acid/TTIP mixture.

1. 10mL TTIP was placed in a polypropylene beaker.
2. 19.2mL glacial acetic acid was added while stirring and the mixture stirred for 20 minutes.
- 35 3. 0.14mL 86% orthophosphoric acid (aqueous) was dissolved in 120mL deionised water. This solution was added to the mixture of TTIP and glacial acetic acid while stirring and the mixture stirred for 40 minutes. A sol with a translucent milky white appearance was formed.

Antimicrobial testing results

The purpose of the antimicrobial testing was to determine the antibacterial activity of a photocatalytic material applied to ceramic tiles against *Staphylococcus aureus* after 6 hours exposure to light as per ISO 27447:2009.

18 ceramic tiles coated with KCS116 and 24 uncoated ceramic tiles were submitted to an independent third party for testing by Kastus Technologies. 6 coated and 9 uncoated control ceramic tiles were randomly selected for testing.

The number of viable bacteria recovered from the tiles at t = 0 and after 6 hours exposure to UV or dark conditions are expressed as colony forming units per ml (cfu/ml). The photocatalytic antibacterial activity value after irradiation (RL) and the photocatalytic antibacterial activity including any effect in the dark (ΔR) are calculated from the logarithmic values for viable bacteria (cfu/ml) according to the formulae in ISO 27447: 2009. These results are presented in Table 2 below.

Summary of Results for <i>Staphylococcus aureus</i>				
Sample	Sample Exposure	Contact Time		Log Values
		0 Hrs	6 Hrs	Log ₁₀
KCS116 coated	UV 0.25mW/cm ²	3.88E+05	3.33E+01	0.47
KCS116 coated	Dark	3.88E+05	1.69E+05	5.12
Uncoated Control	UV 0.25mW/cm ²	3.88E+05	9.67E+04	4.93
Uncoated Control	Dark	3.88E+05	1.04E+05	5.01

Table 2. Antimicrobial testing of coated and uncoated samples

It can be seen from the results outlined in Table 2 that there is a significant reduction in the number of colony forming units following UV exposure observed regarding the formulation coated sample in comparison to the control.

- 5 The log values from the Table 2 were used to calculate RL and ΔR , where the Photocatalytic antibacterial activity RL = 3.46 and the Photocatalytic antibacterial activity including any effect in the dark ΔR = 3.67.

Sample Preparation

- 10 The crystal structure, phase composition, and bandgap of P-doped solution were determined by Raman spectroscopy, X-ray diffraction, and UV-Vis spectroscopy after heating to 700°C, 900°C, 950°C, 1000°C and 1100°C.

- Powders were prepared from each sol by heating samples of approximately 20 mL to 200°C on a hotplate. The dried residue was then heated at a rate of 10°C per minute to the target temperature, held for 1 hour
15 and then allowed to cool naturally to room temperature.

Analysis and Results:

Raman Spectroscopy

- 20 As stated in the background, in order for a TiO₂ surface to be photocatalytic, it must be in the Anatase or Brookite phase (more commonly Anatase). Therefore, the factor which limits the temperature range for firing of a TiO₂ solution, is the temperature at which it will still have enough Anatase present to be a functional photocatalyst. This transition from Anatase to Rutile is
25 also time dependent, however, if time is kept constant across all quality checks, then a comparison can be built up between the abilities of the F-doped and P-doped solutions to maintain Anatase at high temperatures.

Samples of the different levels of P-doping were converted to powder form by calcination at various temperatures. These samples were then examined by

Raman Spectroscopy to determine the presence of Anatase, Rutile and Brookite in them.

5 The Raman measurements were carried out using a laser with excitation wavelength of 532nm (700-800nm sampling depth). The spectra were recorded in two modes, namely line scan and image scan. In the line scan mode, 30 points across a line with integration time of 15s were measured across several areas of the powdered specimen. For Raman imaging, 3600 spectra were averaged in the chosen areas across the sample. This comprehensive Raman sampling ensured the obtained spectra are representative of the powder sample
10 characteristics.

Summary of Raman Results

For reference, the Raman peak position of three natural TiO_2 polymorphs has been tabulated and shown in Table 3. It is noted that in each crystal phase,
15 there is a strong Raman peak which is indicative of the presence of that TiO_2 crystal phase in the sample. If that peak is observed, then other peaks can be assigned accordingly; otherwise, assigning unknown peaks that appear at the wavenumbers close to the values shown in Table 3 to a particular titania crystal phase is incorrect.

Table 3. TiO₂ natural polymorph Raman peak positions.

Wavenumber	Phase	Wavenumber
		137, strong, A _{1g}
		138, weak, B _{1g}
143, very strong, E _g	143, weak, B _{1g}	
		153, very strong, A _{1g}
		159, shoulder, B _{1g}
		172, shoulder, B _{1g}
197, weak, E _g		194, weak, A _{1g}
		214, weak, B _{1g}
	235, broad medium combination band	
		247, medium, A _{1g}
		254, weak, B _{1g}
	273, shoulder	287, weak, B _{1g}
320, very weak, combination band	329, weak, 2 nd order band	320, weak, B _{1g}
		329, weak, B _{1g}
	357, weak, 2 nd order band	
		366, weak, B _{1g}
399, medium, E _g		396, shoulder, B _{1g}
		432, weak, A _{1g}
		435, weak, B _{1g}
	457, strong, E _g	452, weak, B _{1g}
		463, weak, B _{1g}
		476, weak, B _{1g}
		497, weak, A _{1g}
		502, weak, B _{1g}
514, medium, A _{1g} & B _{1g}		
	612, strong, A _{1g}	545, weak, B _{1g}
		584, weak, B _{1g}
639, medium, E _g		618, weak, B _{1g}
665, very weak, combination band		640, strong, A _{1g}
706, weak, B _{1g} overlap		
	826, weak, B _{1g}	

The Raman spectrum of Figure 2 was recorded from a sample fired at 900°C. The most prominent Raman band is the peak at 143.2 cm⁻¹ that is confidently assigned to the Anatase E_g Raman mode. The other Raman peak observed in the spectrum are also assigned to various other Raman modes of Anatase which appear with less intensity.

The spectrum of Figure 3 was recorded from a sample fired at 950°C but cooled in a furnace with faster cooling rate in comparison to the previous specimen. The A refers to Anatase and R denoted Rutile phase in the

spectrum. One can notice that **faster cooling** rate results in **higher** fraction of **Rutile** which could be due to the fact that Anatase is an elongated structure, so the atoms need more time for diffusion along the c axis of the crystal.

5 Figure 4 shows a line scan spectrum averaged over 30 points of data acquisition, showing similar bands to the previous spectrum. One can note that even at **1000°C** there is **still Anatase detectable** in the specimen. To further analyse the distribution of anatase and its fraction, Raman imaging was carried out whose results are shown in Figure 5. The results confirm that Anatase is
10 present in satisfactory quantity over the surface.

Figure 6 shows the line scan averaged spectrum of specimen fired at **700°C**. As expected, the only detectable Raman peaks are related to **Anatase** phase, comprising **%100** of the specimen.

15

Figure 7 displays the averaged Raman line-scan spectrum of **900°C**, clearly showing presence of Anatase phase in the specimen. The very weak almost negligible peaks at $\sim 796\text{ cm}^{-1}$ and $\text{cm}^{-1} > 1000$ are attributed to titanium phosphate phases.

20

Figure 8 shows the Raman spectrum of **950°C** sample averaged over 30 points in a line-scan. The spectrum **only** consists of **Anatase** peaks, implying one-phase nature of this sample.

25 Figure 9 shows the average spectrum of **1000°C** specimen, showing a mixed-phase nature. The medium and strong peaks are assigned as (left to right): 143.1 to Anatase, 234.9 to Rutile, 447.7 to Rutile, 611.3 to Rutile. The peaks at 720 and ~ 1036 are attributed to titanium phosphate phases.

Figure 10 shows the optical microscope image (left) and the scanned area (red square) and the corresponding Raman imaging maps of Anatase and Rutile phases.

5 Figure 11 shows the optical microscope image, total average spectrum, and corresponding Anatase and Rutile maps of the red square marked in the green image. These results suggest that even at a temperature as high as **1100°C**, there is still **noticeable amount of Anatase** present in the specimen.

10 Figure 12 displays the Raman spectrum of sample averaged over 30 points line-scan acquisitions. The spectrum consists of **strong representative Anatase** peaks and some weak peaks at wavenumbers $> 1000\text{ cm}^{-1}$ which are assigned to Ti phosphate phases. The **same behaviour** was observed in the case of specimen **fired at 950°C** (see Figure 13).

15 Figure 14 shows the Raman imaging results from the 1000°C sample. The main point to note is the strong Anatase signal and the titanyl pyrophosphate (TPP) phase. This implies that a higher P content in the sol results in stabilisation of Anatase, while the fraction of TPP phase also increases.

20 Figure 15 shows the Raman imaging results of sample fired at 1100°C. While Rutile makes up the matrix phase of specimen, it is interesting to see that Anatase is still present at such a high temperature. One difference to note is the intensity of TPP phase that has increased in this sample, possibly due to the higher energy input in the system to overcome the energy barrier needed to
25 form TPP phases. Since TPP can act as photocatalyst itself, the overall photocatalytic performance of the system is expected to improve.

X-ray Diffractometry (XRD) Results:

KCS110

5

KCS110 consisted entirely of anatase at 700°C (Figure 16) and 900°C (Figure 17), while at 950°C (Figure 18), the majority phase was rutile. A small minority of anatase was present at 1000°C (Figure 19) and at 1100°C (Figure 20), the only phase detected was rutile. The peak resolution increased between 10 700°C and 900°C. It is not clear whether this was due to the elimination of a small quantity of residual amorphous material, or reduced peak spreading caused by grain growth.

KCS111

15

As was the case with KCS110, KCS111 was composed entirely of anatase at 700°C (Figure 21) and 900°C (Figure 22), but at 950°C (Figure 23), anatase remained the majority component, with only a small proportion of rutile, in approximately the reverse proportion to that seen in KCS110. After heating to 1000°C (Figure 24), only a small fraction of anatase remains and at 1100°C 20 (Figure 25), the sample is entirely rutile.

KCS112

After heating to 700°C (Figure 26), KCS112 appears to be composed of 25 anatase, but the spectrum shows substantially more peak spreading than was the case for KCS110 or KCS111. After heating to 900°C (Figure 27), associated with the anatase structure are more clearly defined, but a second phase is clearly present. It has not yet been established whether this is a phosphorus oxide, or a titanium phosphate. At 950°C (Figure 28), the spectrum continues to

evolve, with peaks consistent with a composition containing at least three phases, anatase, rutile and the third phase that was appearing at 900°C.

At 1000°C (Figure 29), the spectrum is overly complex. A multitude of peaks, many of which were not present at 950°C, indicates that as well as rutile and a small fraction of anatase, there are at least two other phases present. Given the composition of the powder, it is reasonable to postulate that these are a mixture of titanium phosphates. After heating to 1100°C (Figure 30), the spectrum is simpler again, with peaks indicating that the sample contains only rutile and one or more titanium phosphates, distinct from the phase that formed at 900°C.

UV-Visible Spectroscopy and band gap calculations

Samples were prepared for UV-visible spectroscopy, by mixing approximately 1% of the powders calcined at 700°C and 900°C in dry potassium bromide, grinding to a fine powder and pressing into discs in a 13mm pellet die. Spectra (Figures 31 – 37) were collected in transmission mode over a range of 600nm to 250nm, using a Shimadzu 1800 spectrophotometer. Spectra were plotted as a function of absorbance against wavelength and band gap energies were calculated by fitting tangents to the high transparency part of the spectrum in visible wavelengths and the range over which the material underwent a transition from transparent to opaque. The wavelength λ , at the intersection of the two tangents was taken as the onset of the transition from transparent to opaque and the band gap energy calculated from the formula $e = \lambda/1236$, where $1236 = hc$.

Results are given in the Table 4 below.

Temp. (°C)	KCS110		KCS111		KCS112		KCS117		KCS118	
	Absorption edge wavelength h nm	Band gap energy eV	Absorption edge wavelength h nm	Band gap energy eV	Absorption edge wavelength h nm	Band gap energy eV	Absorption edge wavelength h nm	Band gap energy eV	Absorption edge wavelength h nm	Band gap energy eV
700°C	397.88	3.11	397.03	3.11	396.28	3.12	394.38	3.13	385.01	3.21
900°C	397.73	3.11	393.05	3.15	364.05	3.40				
* KCS112 showed a spectrum in which the absorbance increased by approximately 0.4 over a range of 20nm, then continued to increase smoothly and gradually in the UV range. This value is the extrapolated intercept of this UV absorption range into the visible range.					*428.77	*2.89				

Table 4. UV-Visible Spectroscopy and band gap calculations

5 The words comprises/comprising when used in this specification are to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

Claims

1. A process for the preparation of an antimicrobial coating solution, the process comprising the steps of:
 - (i) mixing a chelating agent with a titanium alkoxide and a phosphorylating agent; and
 - (ii) adding an aqueous solution to the mixture formed from step (i).
2. A process according to claim 1, wherein the aqueous solution is added in step (i) and the phosphorylating agent is added in step (ii)
3. A process according to claim 1, wherein the aqueous solution and the phosphorylating agent are added in step (ii)
4. A process according to claims 1 - 3, wherein the chelating agent is a carboxylic acid.
5. A process according to claim 4, wherein the carboxylic acid is selected from the group consisting of formic acid, propionic acid, butanoic acid and acetic acid.
6. A process according to claim 5, wherein the carboxylic acid is acetic acid.
7. A process according to claim 6, wherein the acetic acid is in the form of glacial acetic acid.
8. A process according to claim 7, wherein the amount of glacial acetic acid used is in the range 1 to 40 wt%, preferably in the range 1 to 20% and most preferably, in the range 2 to 10 wt%.
9. A process according to claims 1 - 3, wherein the titanium alkoxide is selected from the group consisting of titanium isopropoxide, titanium ethoxide, titanium methoxide and titanium butoxide.

10. A process according to claim 9, wherein the titanium alkoxide is titanium isopropoxide.
11. A process according to claim 10, wherein the amount of titanium isopropoxide used is in the range 4 to 15 wt %, preferably 6 to 12 wt%.
12. A process according to claims 1 - 3, wherein the phosphorylating agent is selected from the group consisting of orthophosphoric acid, phosphorus pentoxide, ammonium dihydrogen phosphate and diammonium hydrogen phosphate.
13. A process according to claim 12, wherein the phosphorylating agent is orthophosphoric acid.
14. A process according to claim 13, wherein the amount of orthophosphoric acid used is in the range in the range 0.0001 to 1 wt%, preferably in the range 0.002 to 0.005 wt% .
15. A process according to claims 1 - 3, wherein the amount of water in the solution is at least 30% by wt.
16. A process according to claim 15, wherein the amount of water used is in the range 30 wt% to 99.5 wt%, preferably, in the range 40 wt% to 99 wt%; and most preferably, 50 to 95 wt%.
17. A process according to claim 15, wherein the aqueous solution comprises an organic solvent.
18. A process according to 15, wherein the aqueous solution comprises only water.
19. A process according to claim 15, wherein the organic solvent in the aqueous solution is in the range of 0 – 20% by weight.

20. A process for the preparation of an antimicrobial coating solution according to any preceding claim, comprising the step of, after step (ii) as recited in claims 1 – 3, (iii) the addition of a dispersing agent.
- 5 21. A process according to claim 20, wherein the dispersing agent is selected from one or more of the group comprising: Disperbyk 180, Disperbyk 2060, Disperbyk 2061, Disperbyk 2062, Disperbyk 2080, Disperbyk 2081 and Disperbyk 2205.
- 10 22. A process according to any preceding claim, wherein the process is carried out at a temperature between 10 and 65 °C.
23. A process for making an antimicrobial powder comprising the initial step of preparing a solution in accordance with any preceding claim, evaporating the
15 solvents from the solution and then annealing the residue at a temperature between 300 °C and 1400 °C.
24. A method of preparing an antimicrobial coating composition comprising the step of mixing an antimicrobial powder as prepared by the process of claim 23
20 with a coating solution as prepared by the process of claims 1, 2 or 3.
25. An antimicrobial coating composition obtained by the method according to claim 24, wherein the coating composition is UV and visible light activated.
25
26. An antimicrobial coating composition according to claim 25 which exhibits antimicrobial activity under both UV and visible light and in reduced light.
27. An antimicrobial coating composition according to claim 26, which is stable
30 at temperatures up to 1400 °C.

28. An antimicrobial coating composition comprising a hydrolysed phosphorus-sol.
29. An antimicrobial coating comprising a transparent phosphorus-doped titania
5 coating.
30. An antimicrobial coating composition comprising phosphorus-doped titanyl acetate.
- 10 31. An antimicrobial coating composition according to claim 30 wherein the phosphorus-doped titanyl acetate is hydrolysed.
32. A method for coating a substrate, the method comprising the steps of
15 (i) depositing an antimicrobial coating solution prepared according to the process of any one of claims 1 to 23 or an antimicrobial coating composition according to any one of claims 25 to 27, on a substrate;
(ii) drying said coating; and
(iii) exposing the coated substrate to a temperature above 300°C for a
20 period of time in the range 20 minutes to 30 hours.
1.
33. A method according to claim 32, wherein the coated substrate is exposed to a temperature in the range 300°C to 1400°C, preferably 350°C to 1100°C.
- 25 34. A method according to any one of claims 1 to 24, wherein the mixture from step (i) is stored prior to the execution of step (ii).
35. A method according to claim 34, wherein the step of storing comprises packaging the mixture for transport.

36. A method according to any one of claims 1 to 24 wherein the coating is deposited by a method selected from the group consisting of spraying, dipping, roller, brush, electrostatic and spin-coating.

5 37. A coated substrate comprising an antimicrobial coating prepared by the process according to any one of claims 1 to 23 or an antimicrobial coating composition according to any one of claims 24 to 26.

38. A coated substrate according to claim 37, wherein the substrate is selected
10 from the group consisting of glass and related composite materials, ceramics, plastic, cement and clay.

39. A coated substrate according to claim 38, wherein the substrate comprises a metal, optionally stainless steel or aluminium or an alloy thereof.

15

40. A process for the preparation of an antimicrobial coating composition substantially as hereinbefore described and/or exemplified.

41. An antimicrobial coating composition substantially as hereinbefore
20 described and/or exemplified.

42. A coated substrate substantially as hereinbefore described and/or exemplified.

25

Abstract

P-doped surface coatings and process of preparation thereof

5 A process for the preparation of an antimicrobial P-doped coating solution is described. The process for the preparation of the antimicrobial coating solution uses non-volatile and non-oxidising phosphoric acid. The antimicrobial coatings are active in both the UV and visible light spectrum.

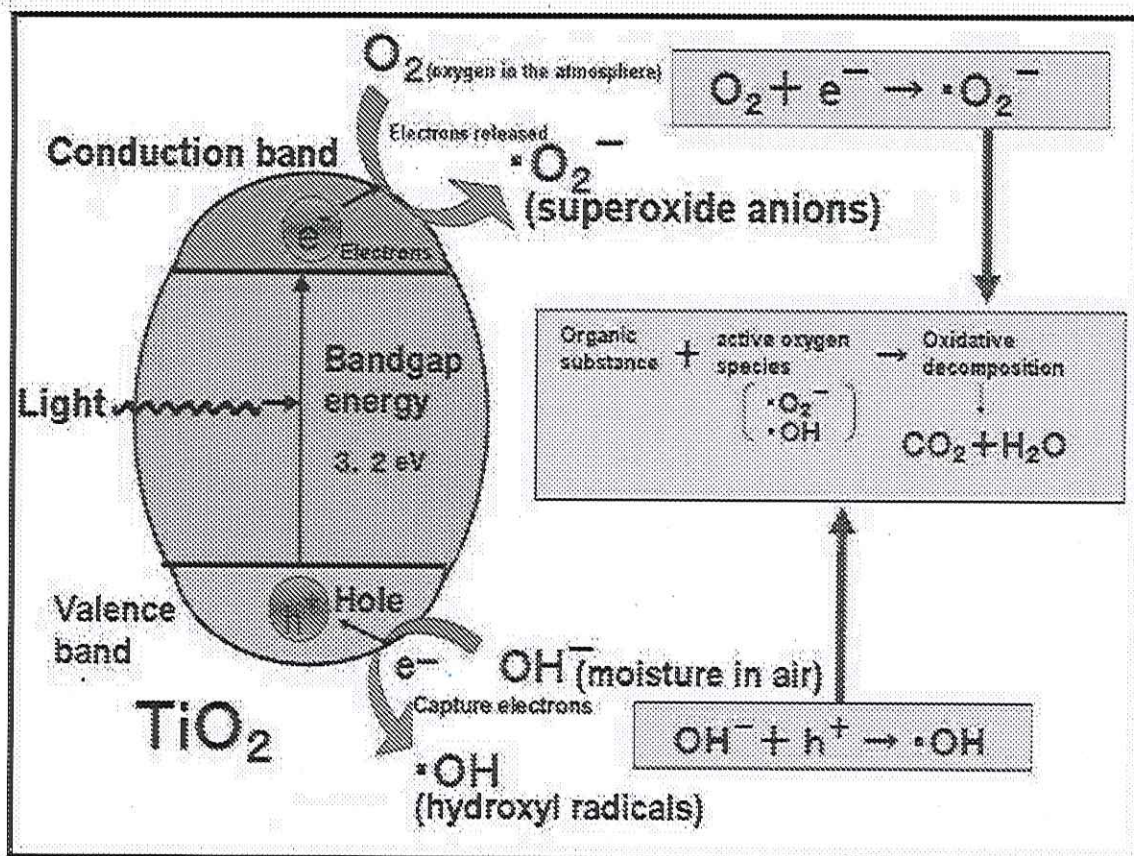


Figure 1

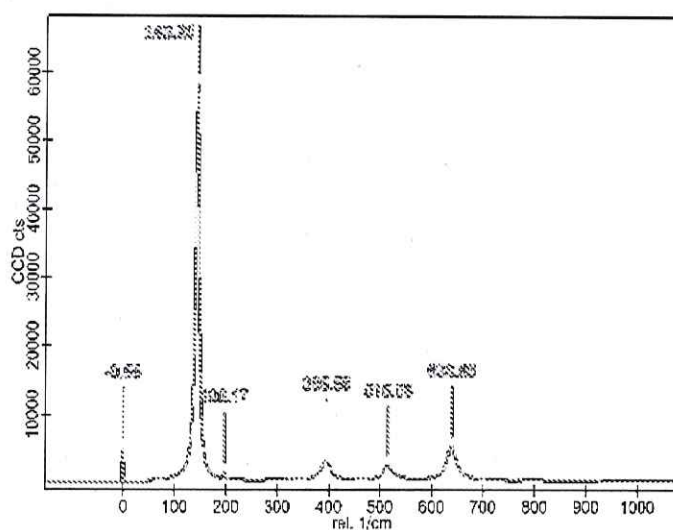


Figure 2

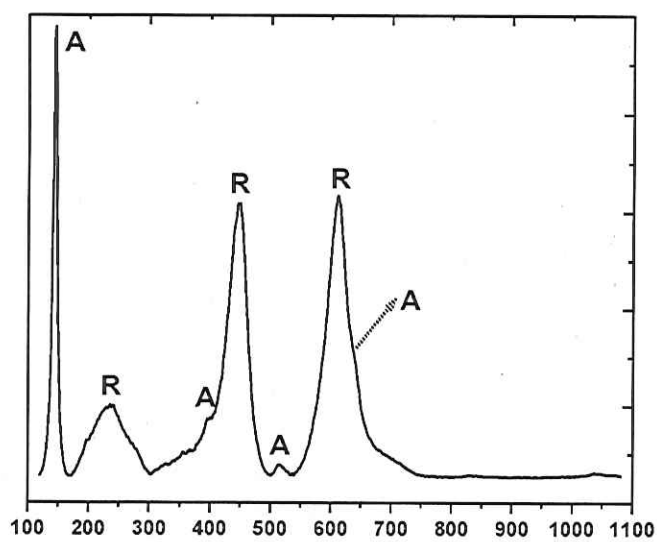


Figure 3

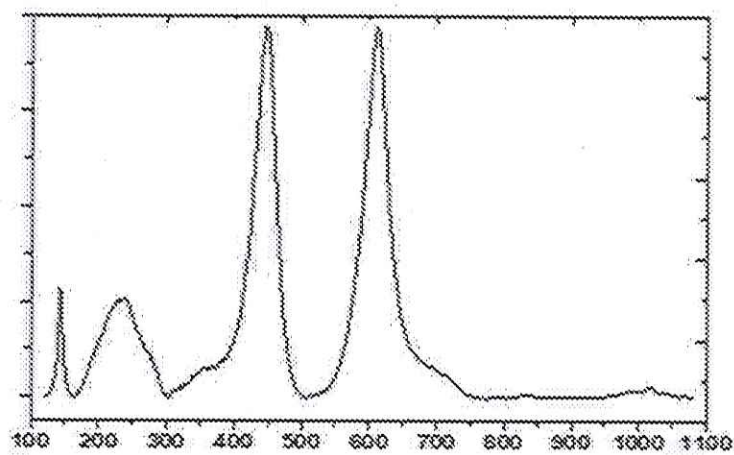


Figure 4

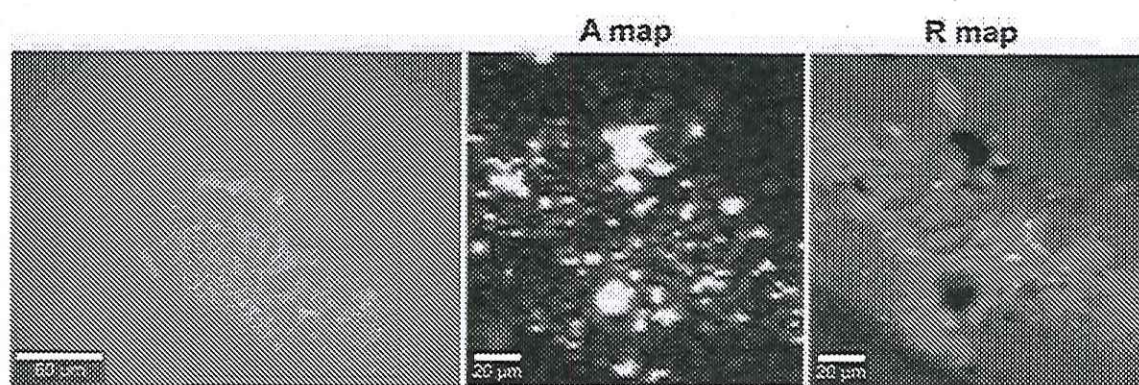


Figure 5

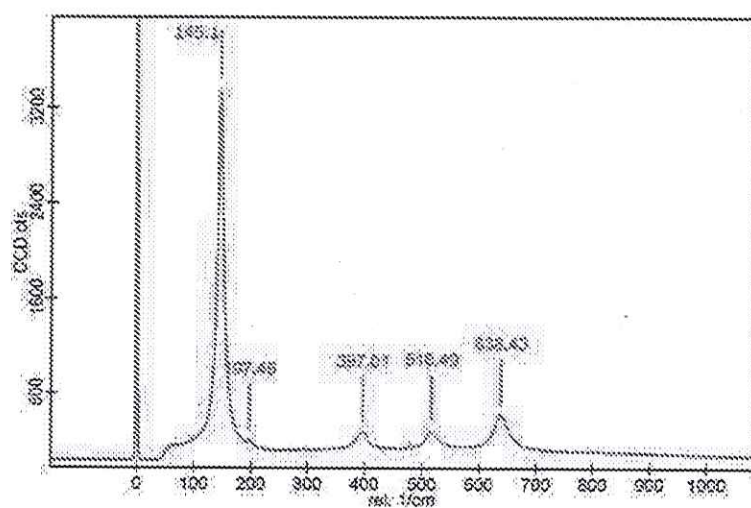


Figure 6

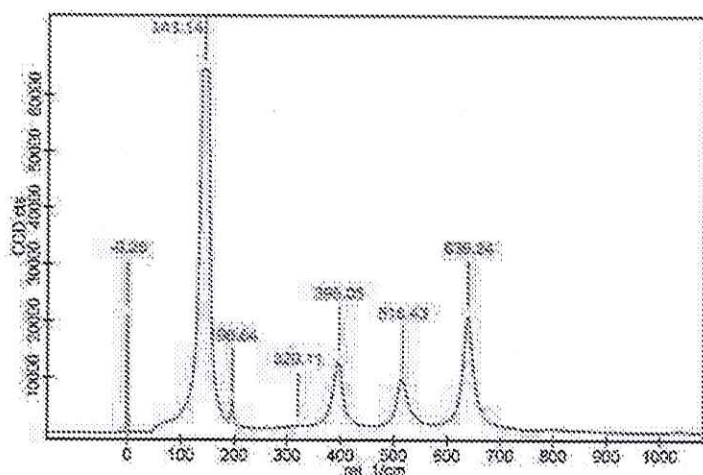


Figure 7

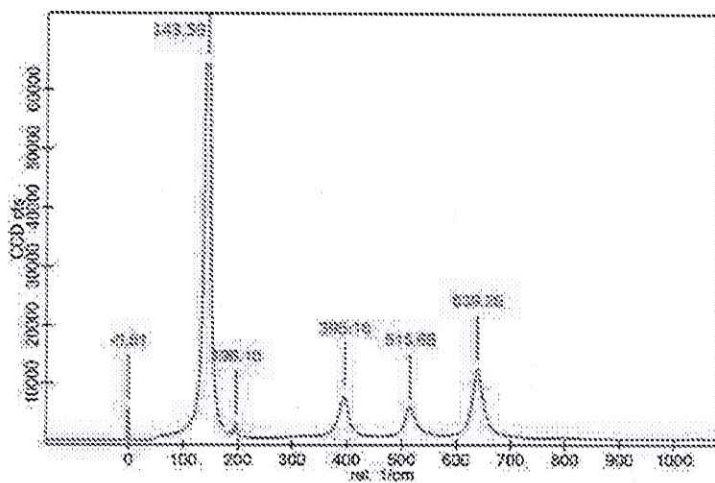


Figure 8

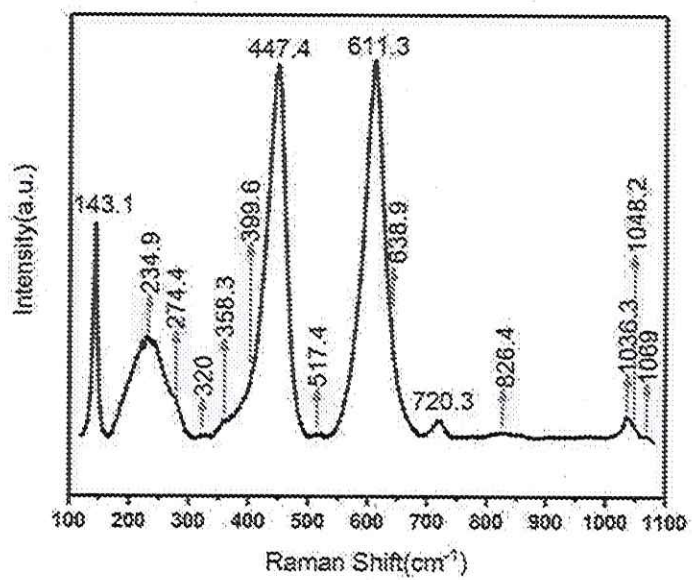


Figure 9

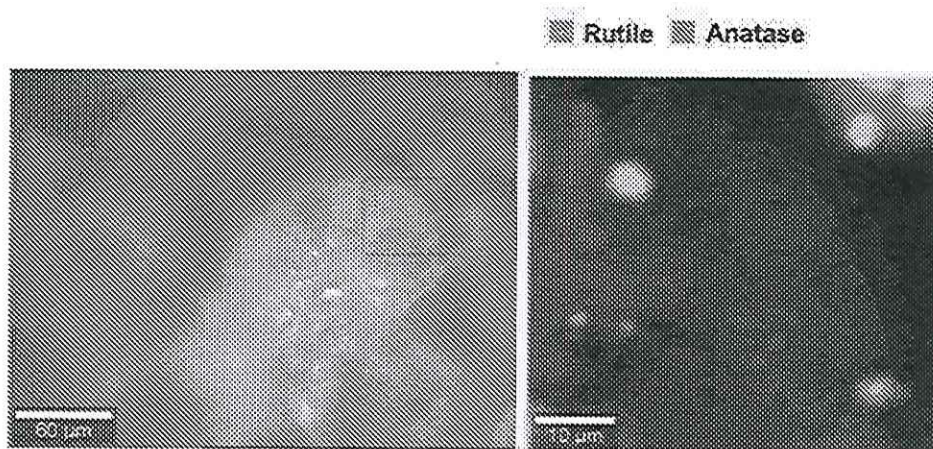


Figure 10

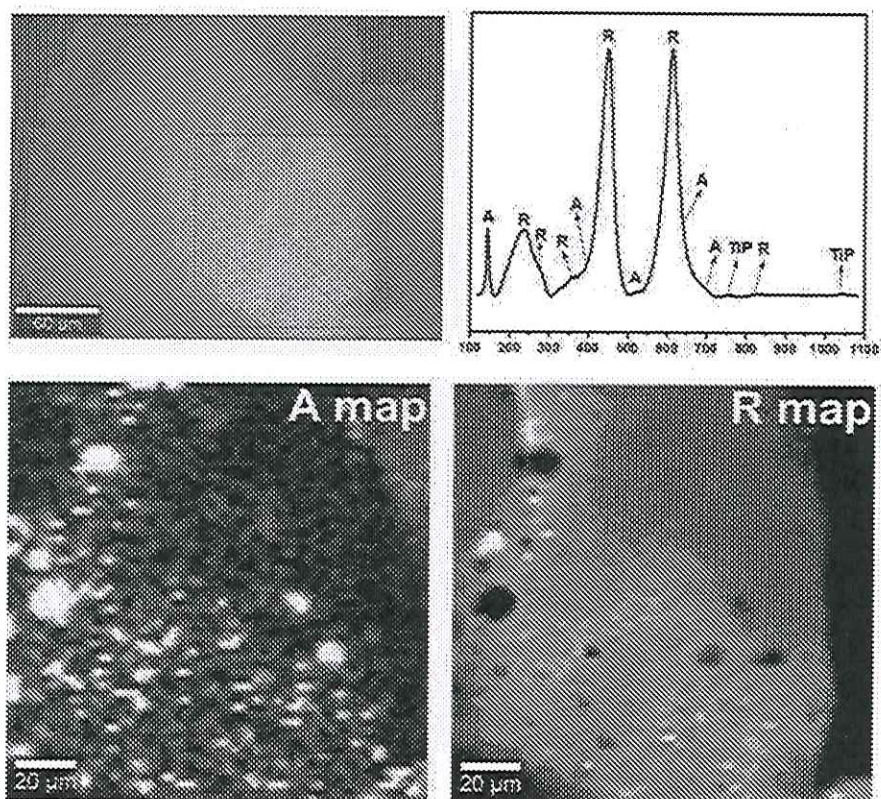


Figure 11

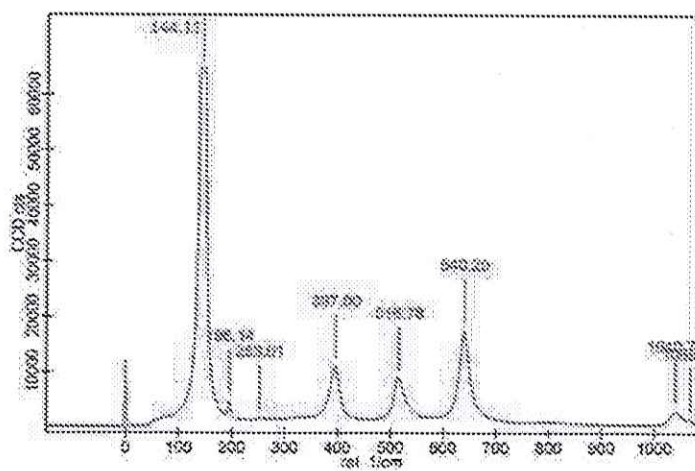


Figure 12

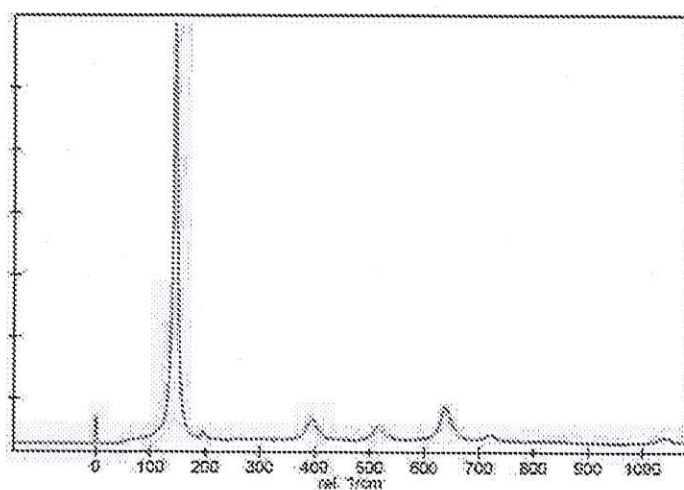


Figure 13

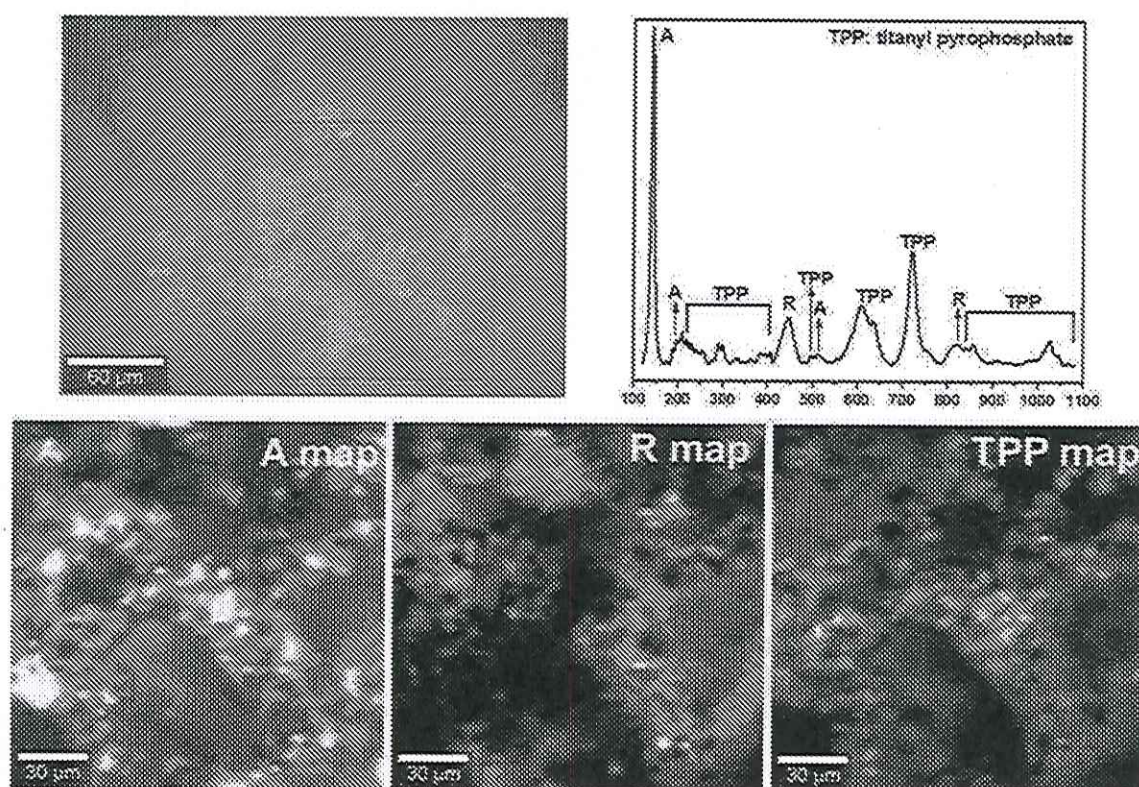


Figure 14

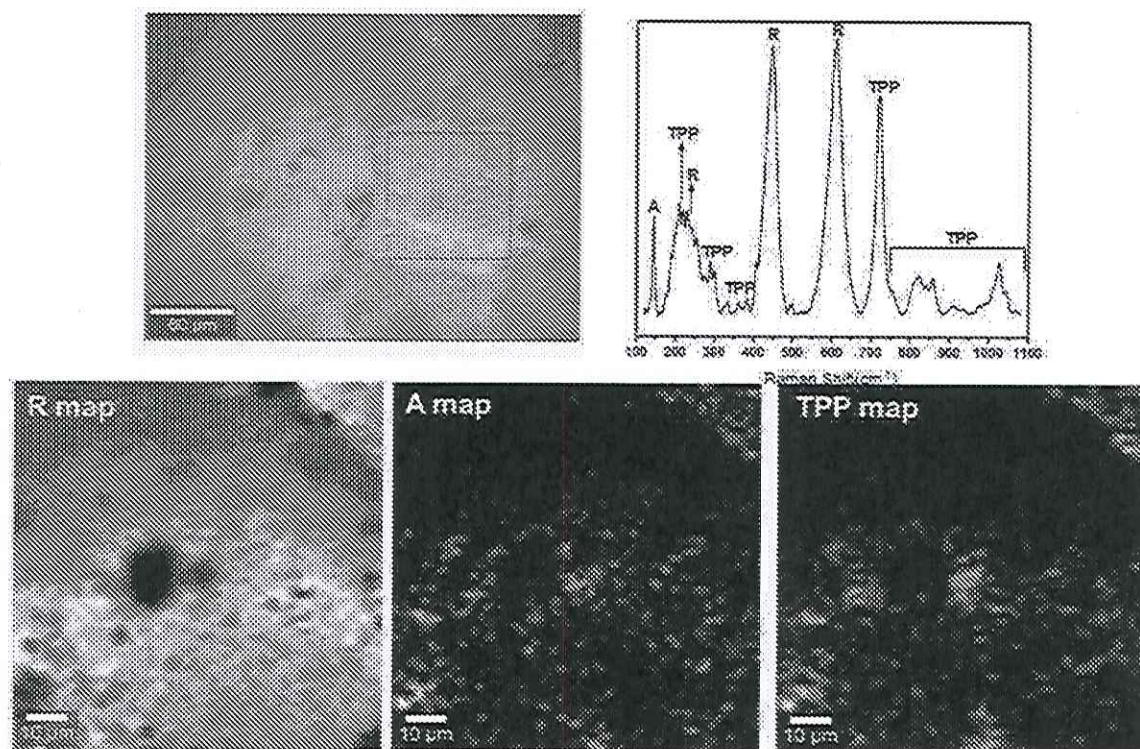


Figure 15

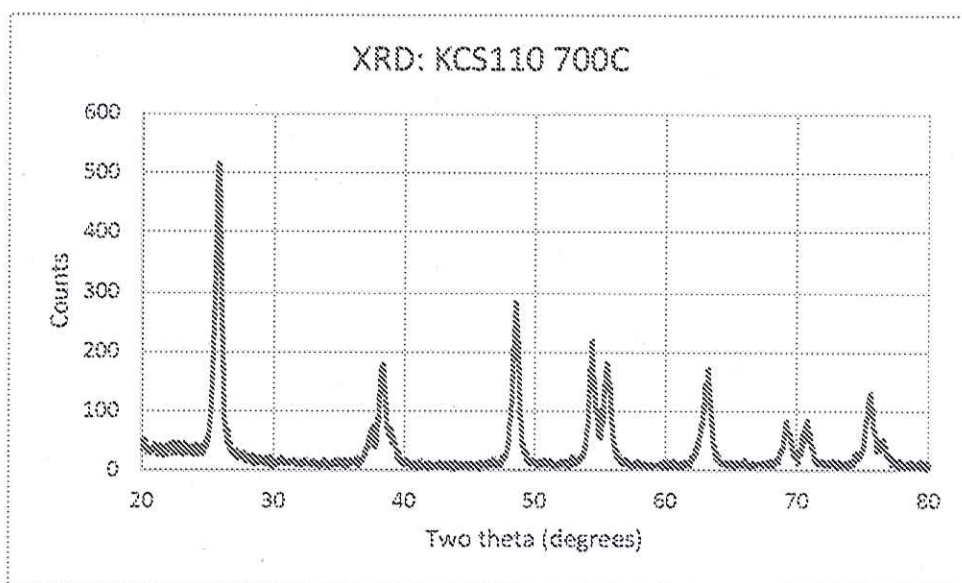


Figure 16

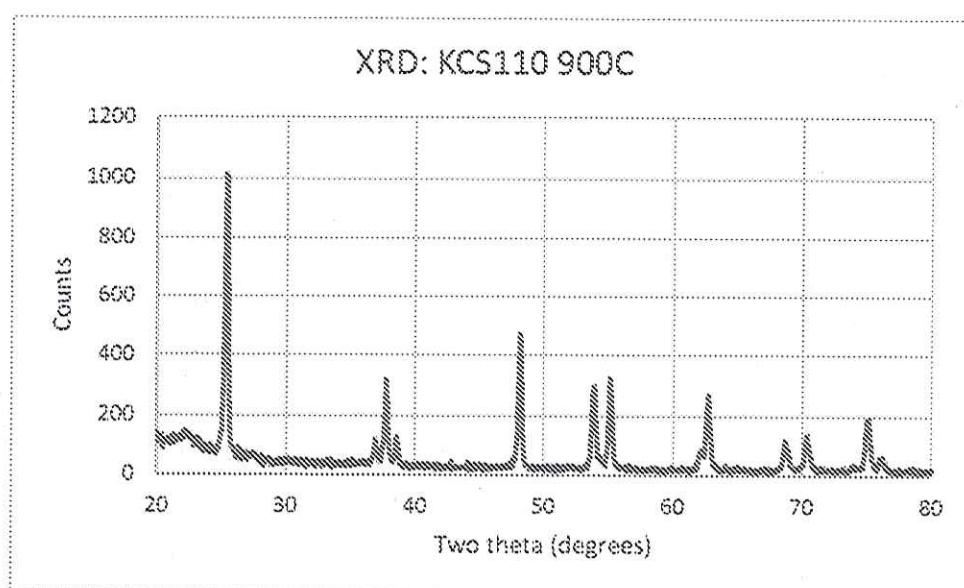


Figure 17

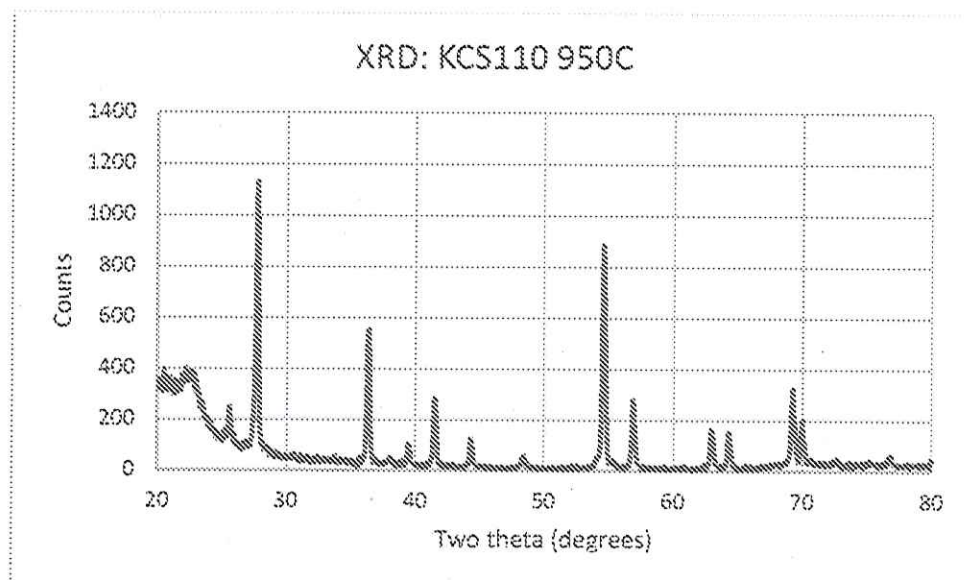


Figure 18

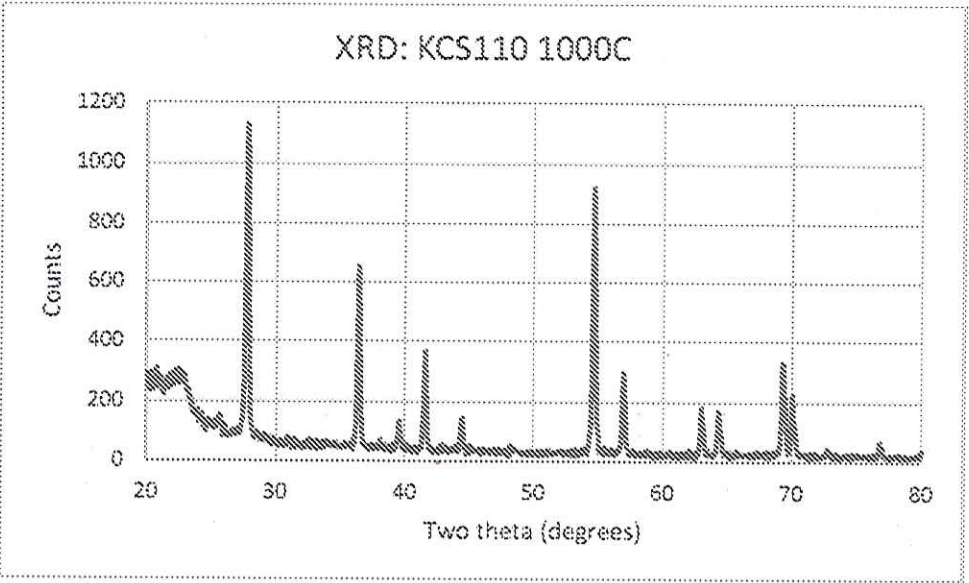


Figure 19

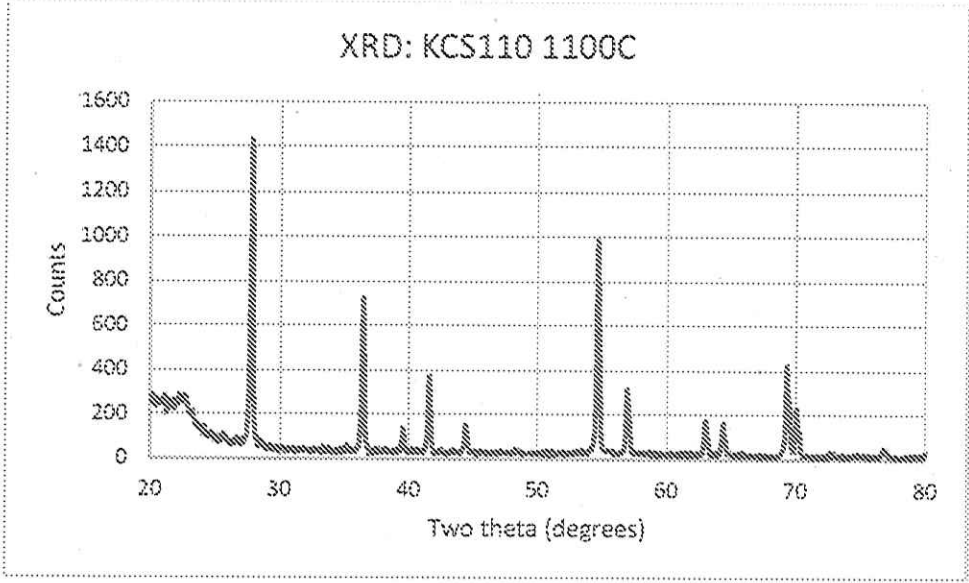


Figure 20

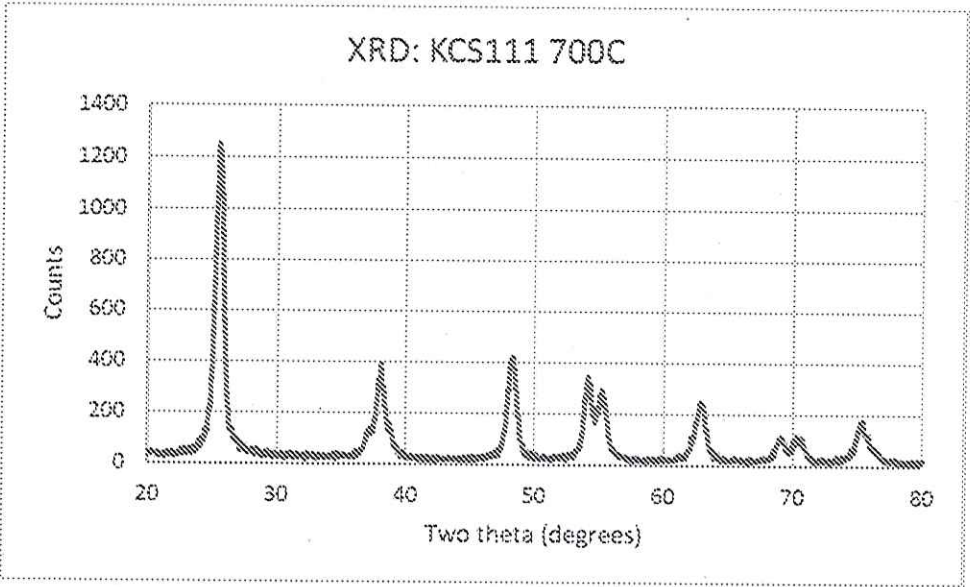


Figure 21

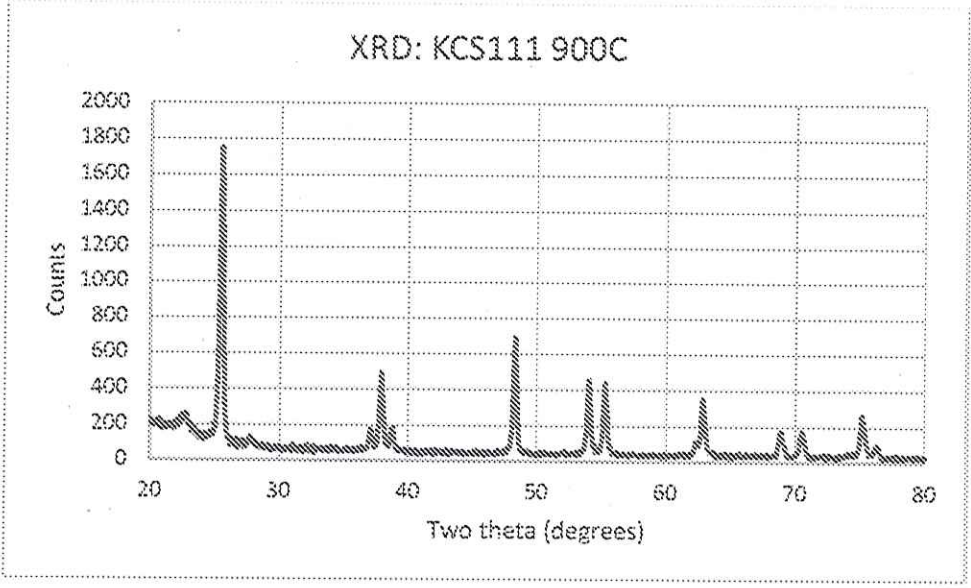


Figure 22

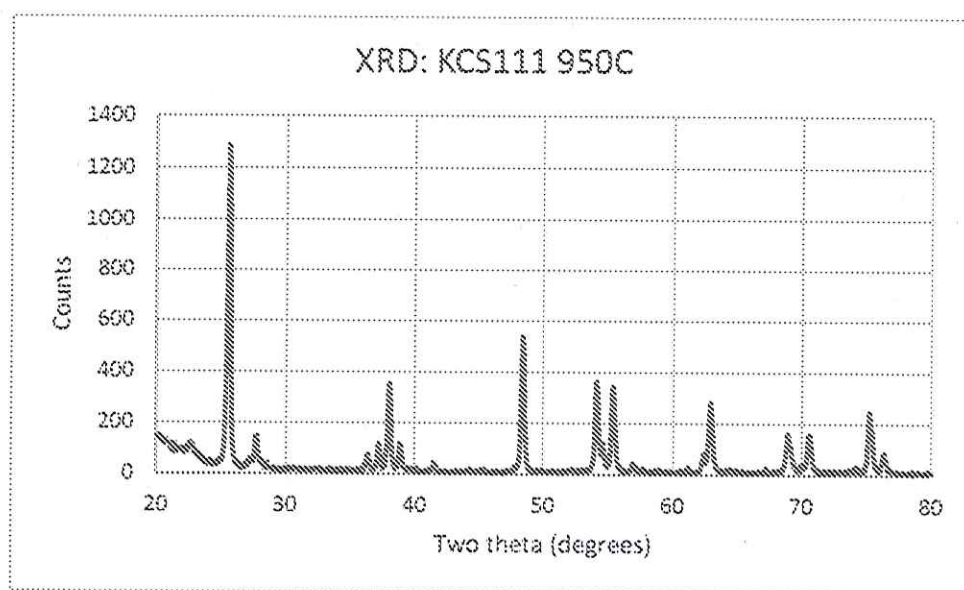


Figure 23

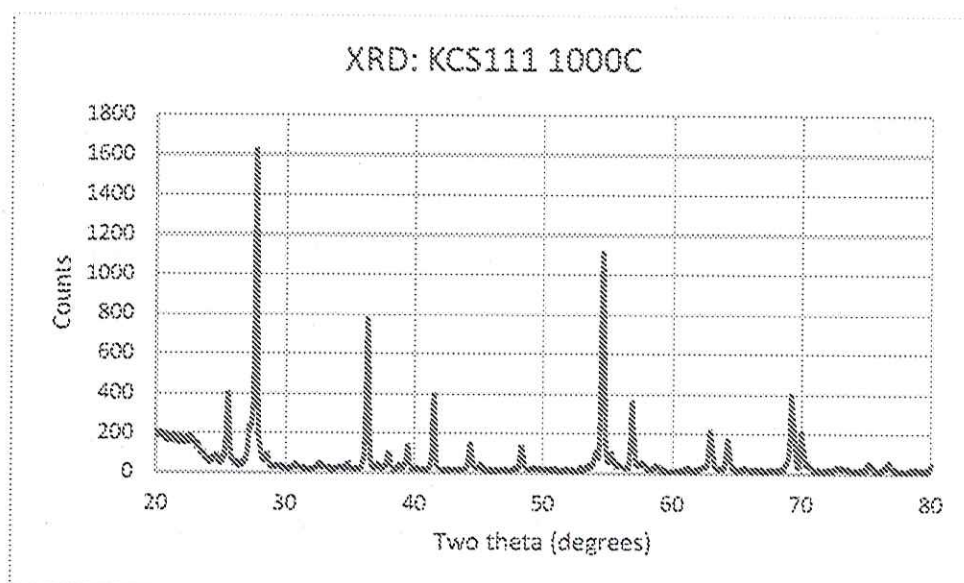


Figure 24

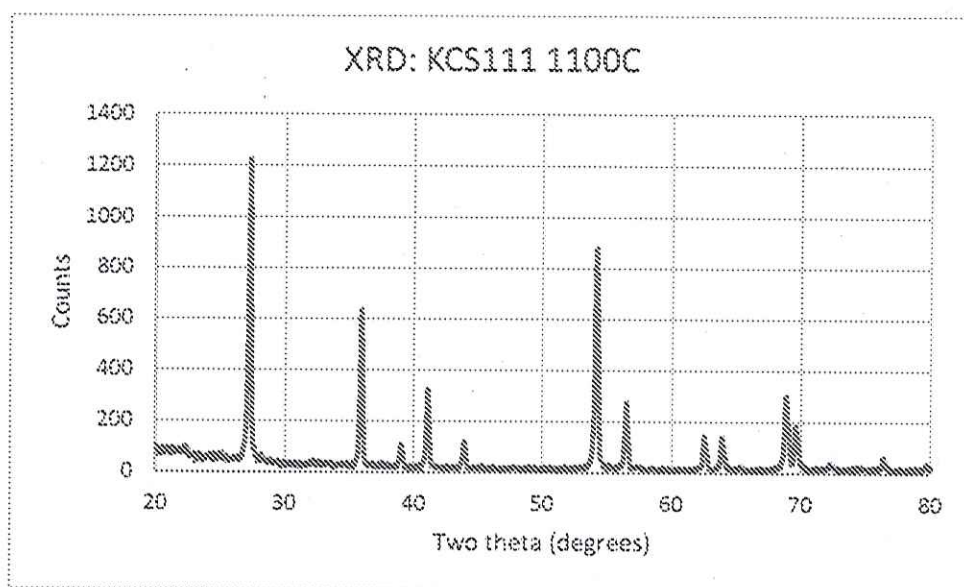


Figure 25

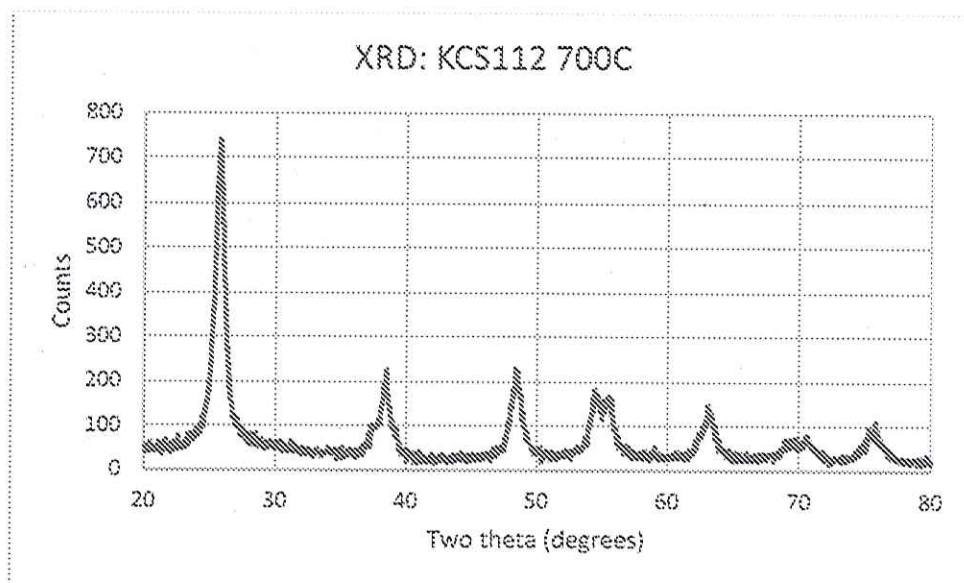


Figure 26

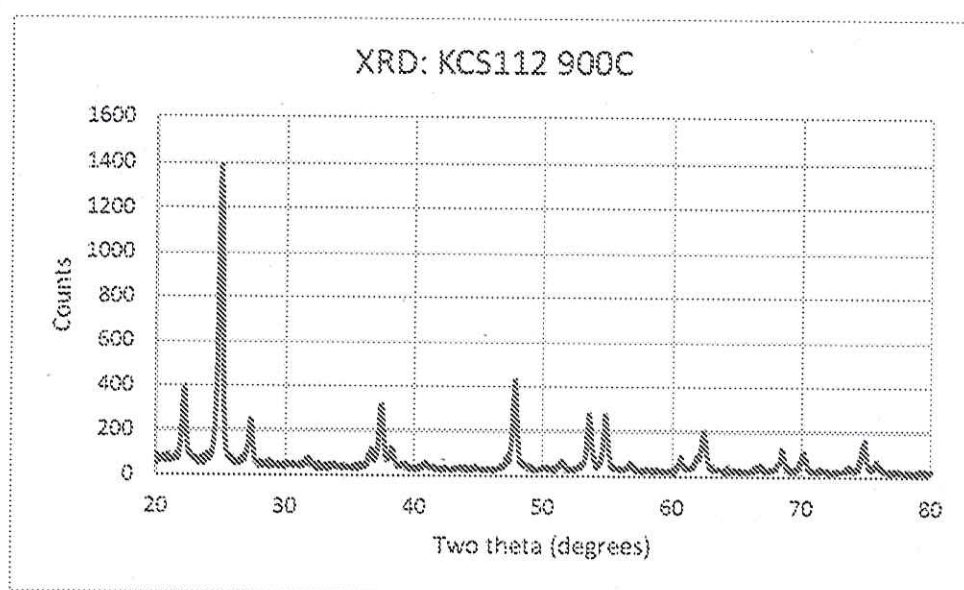


Figure 27

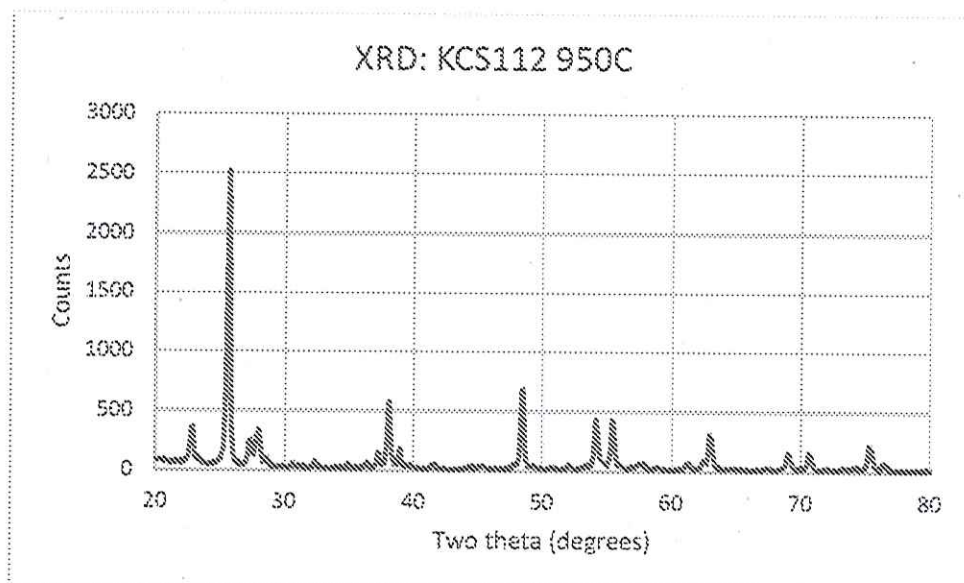


Figure 28

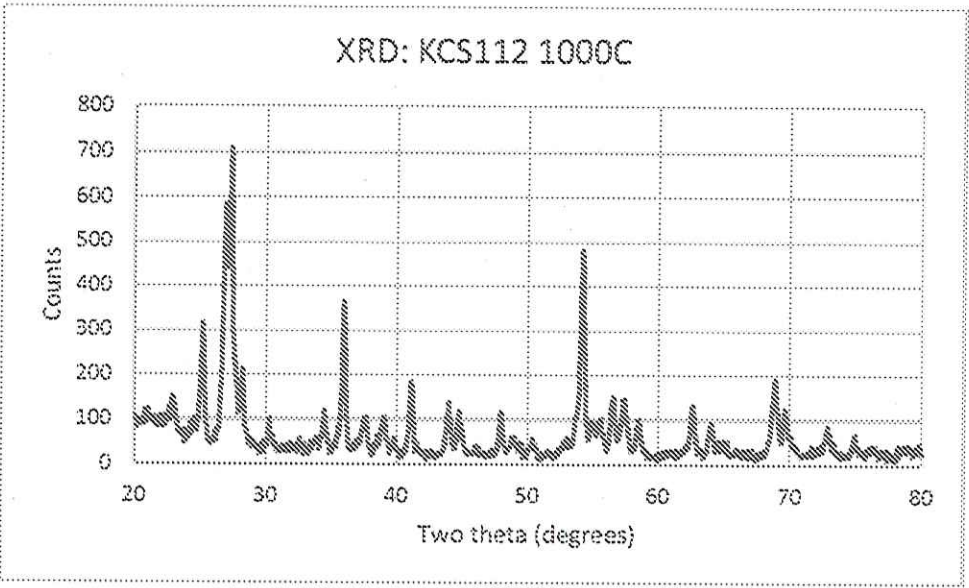


Figure 29

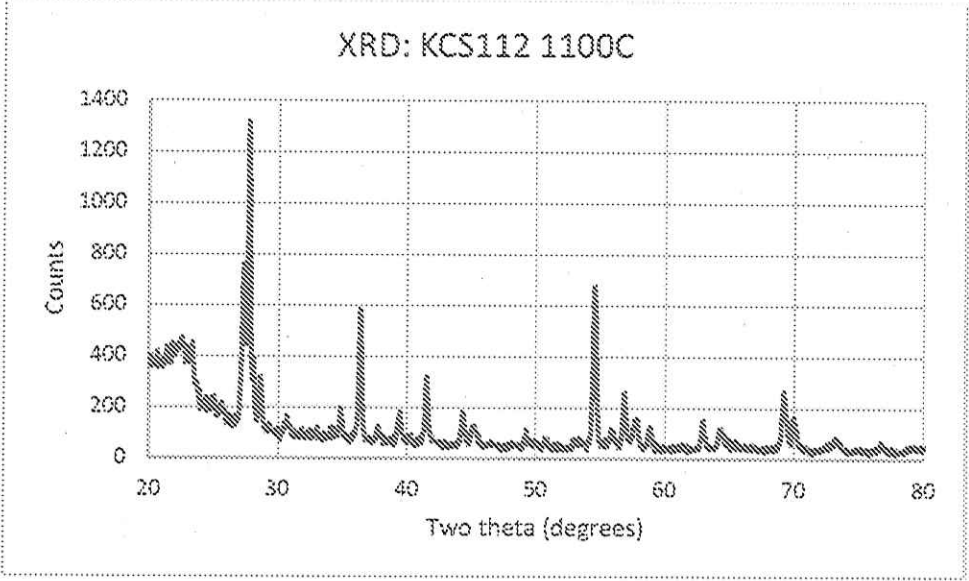


Figure 30

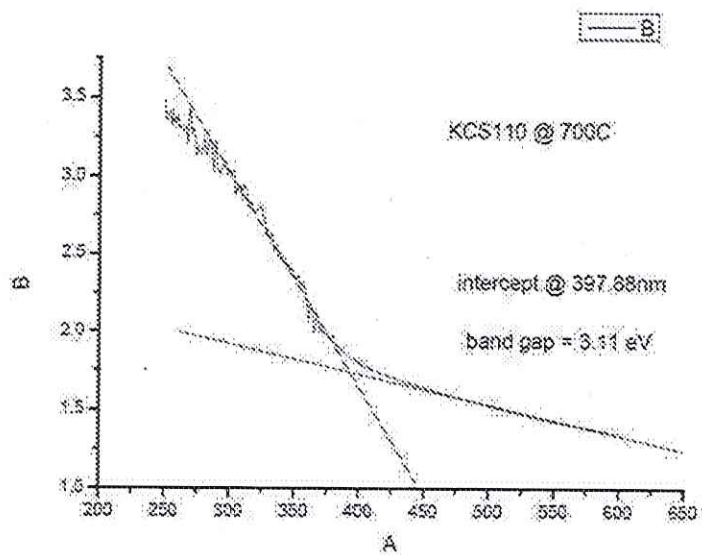


Figure 31

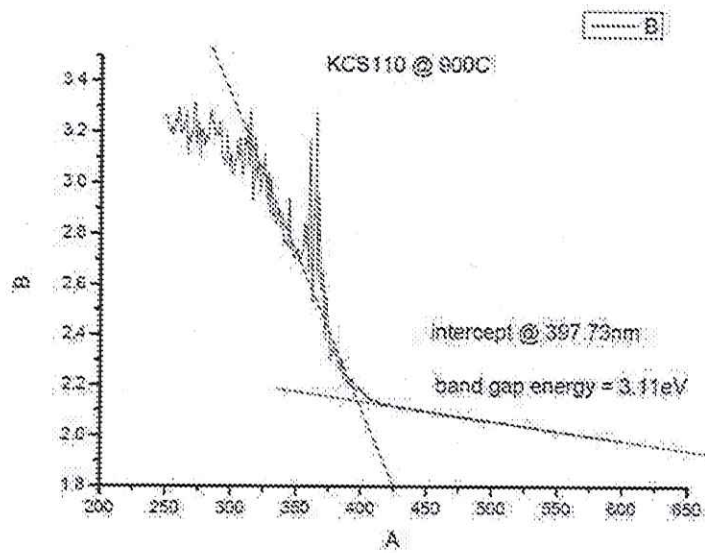


Figure 32

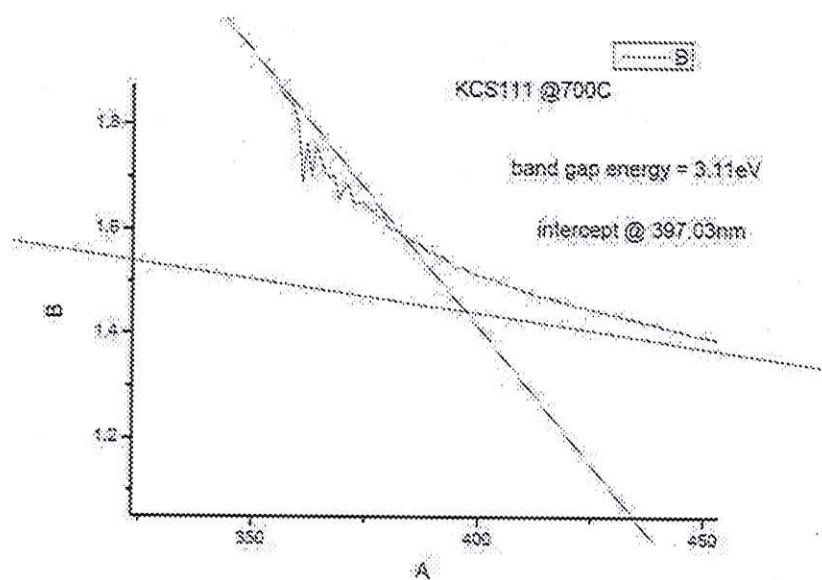


Figure 33

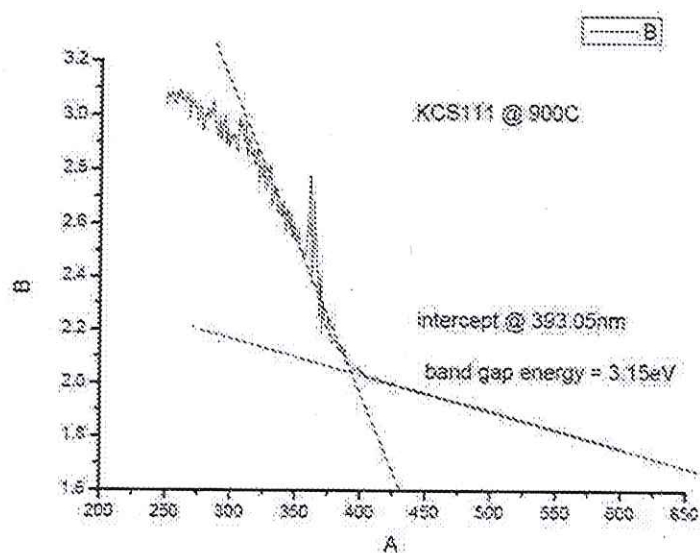


Figure 34

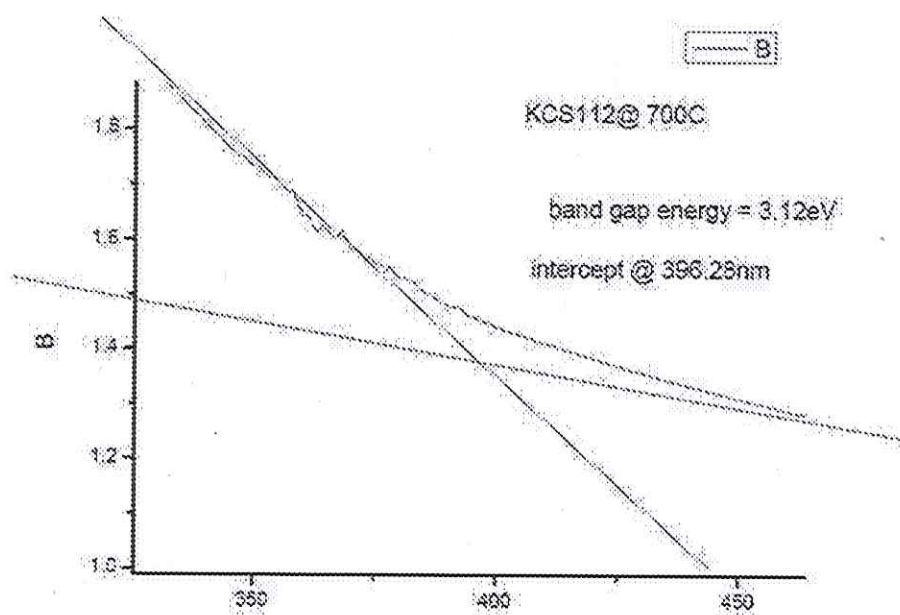


Figure 35

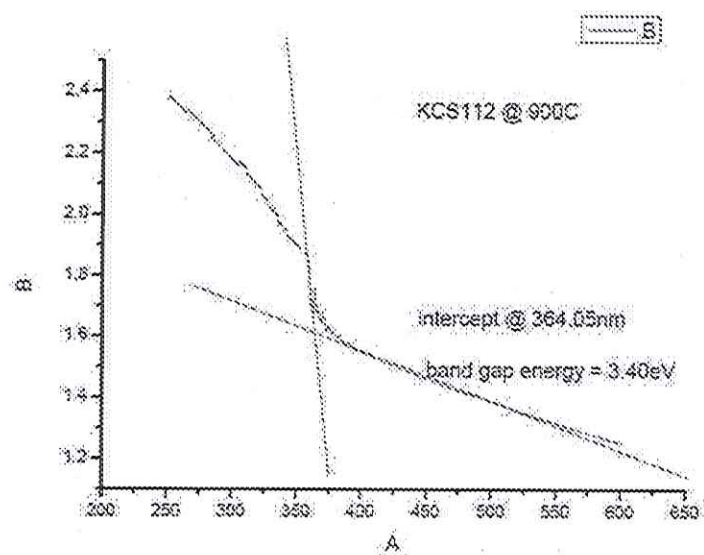


Figure 36

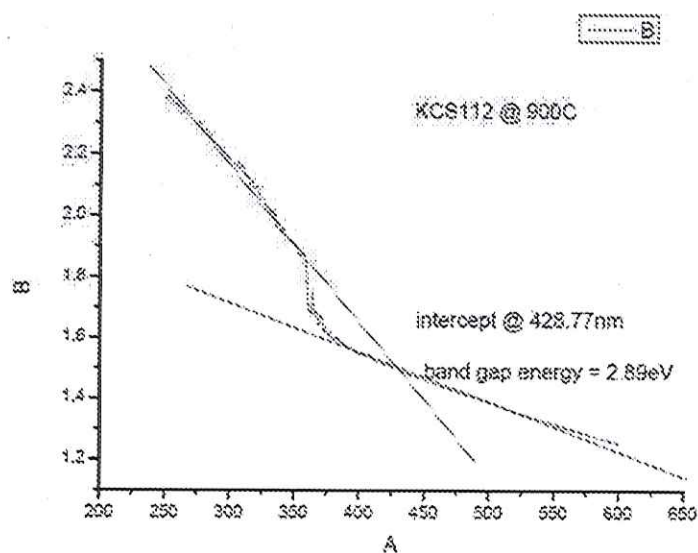


Figure 37

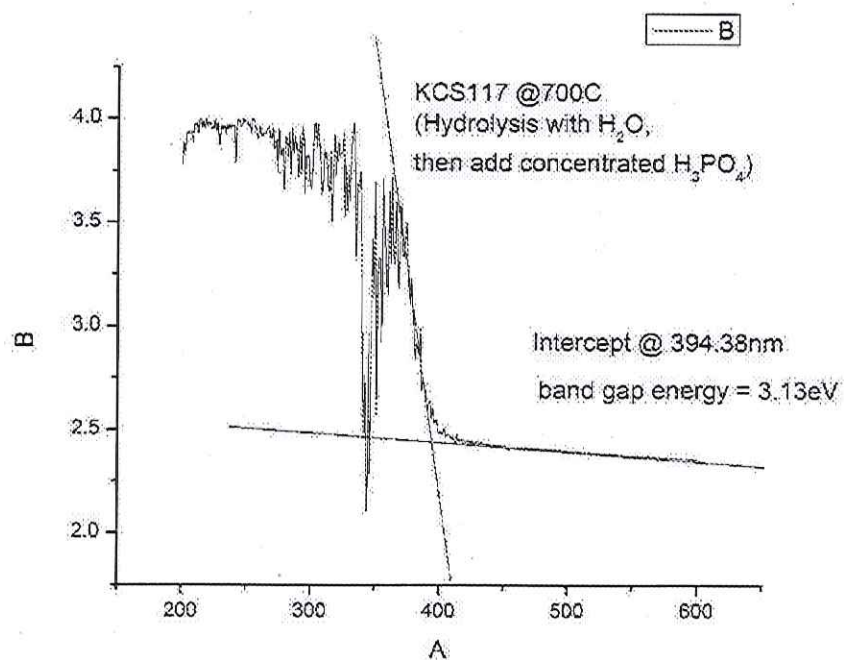


Figure 38

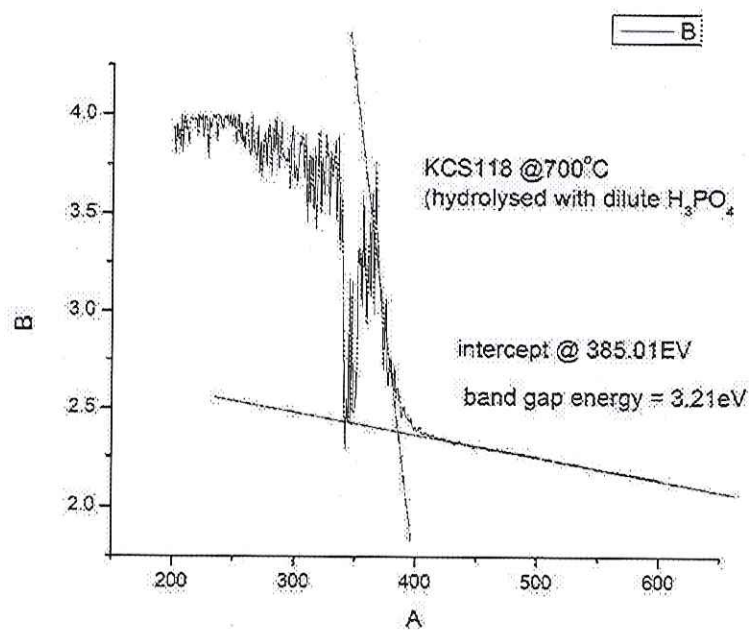


Figure 39