Australian Government
National Measurement Institute

XRD phase analysis of TiO_2 sunscreens

NMI Nanometrology
nano@measurement.gov.au

For:	Dr Gregory Crocetti Friends of the Earth Australia 312 Smith Street Collingwood VIC 3066
Reference:	Q122439
Description:	XRD phase analysis of TiO_2 sunscreens
Maker:	Various. Please see Section 2 of report for sample listing.
Date of Receipt:	All samples received 6/9/12 except Coco Island WHITE ZINC CREAM, received 14/9/12
Serial Number:	M122439
Previous Examination:	None
Date(s) of Test:	2/10/12 – 5/10/12, 11/10/12

For further information contact: Dr Victoria Coleman, Phone: (02) 8467 3820

The meaning and use of specific terms and expressions common to dispersion science and technology used throughout this study are defined as per Special Publication 960-3 of the National Institute of Standards and Technology.[1]
Certain trade names and company products are mentioned in the text in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Measurement Institute, nor does it imply that the products are necessarily the best available for the purpose.

[1] V. A. Hackley and C. F. Ferraris, *The Use of Nomenclature in Dispersion Science & Technology*. NIST Recommended Practice Guide, NIST SP 960-3 (2001).
Available at www.ceramics.nist.gov/ftproot/PracticeGuides/960-3/SP960-3.pdf
(accessed 18 October 2012).

Table of Contents

List of symbols and abbreviated terms used in this report

XRD	X-ray diffraction
JCPDS	Joint Committee on Powder Diffraction Standards

1. Scope

This report presents powder X-ray diffraction (XRD) phase analysis of the titanium dioxide (TiO_2) inorganic particulate fraction extracted from eight commercial sunscreens by washing and centrifugation.

2. Sample list

Table 1: Details of samples received, including lot number, sample reference number, stated TiO_2 mass fraction and list of relevant ingredients.

Product	Lot number	Sample reference number[2]	Stated TiO_2 mass fraction (%)	Other inorganic ingredients
Clarins Paris, *UV PLUS* *(Ecran Protecteur Jour Aux Extraits de Thé Blanc)* SPF 30+ Oil-Free, Protective Day Screen Lotion with White Tea Extracts 30 mL	205006	M122439_001	8.1	not listed
Cancer Council, *Kids sunscreen,* *Very high protection for delicate skin.* Fragrance free. SPF 30+ UVA UVB Broad spectrum 4 HOURS Water Resistant 110 mL	BOO89	M122439_002	2.5	not listed
KEY SUN *WHITE ZINKE* SPF 30+ 4HRS Water Resistance UVA Broad Spectrum UVB 50 g NET	68007B	M122439_003	4	zinc oxide (320 mg/g)
NIVEA SUN *Kids Swim & Play* *Protective Lotion* SPF 30+ VERY HIGH PROTECTION Broad Spectrum UVA+UVB Filters With Panthenol Protects the skin barrier 4 h water resistant 150 mL	B12470577	M122439_004	6	not listed
L'ORÉAL Paris *infallible make-up* *ADVANCED NEVER FAIL MAKEUP* SPF 20 SUNSCREEN 18 HR SMOOTH BLEND COMFORT 30 ml Natural Buff 606	20H302	M122439_005	1.75	iron oxides
COVERGIRL *natureluxe luxury touched by nature la richesse de la nature* SPF 10 FPS sunscreen écran solaire 304 liquid silk foundation fond de teint liquide soyeux 30 mL	11681722D0	M122439_006	2.6	talc iron oxides

[2] Internal NMI code given to sample.

Product	Lot number	Sample reference number[2]	Stated TiO_2 mass fraction (%)	Other inorganic ingredients
COVERGIRL *natureluxe luxury touched by nature la richesse de la nature* SPF 10 FPS sunscreen écran solaire 304 liquid silk foundation fond de teint liquide soyeux 30 mL	11681722D0	M122439_007	2.6	talc iron oxides
Australis powder CREAM Make-up tan 41003	1J1	M122439_008	not listed	zinc oxide silica mica
Australis powder CREAM Make-up disc beige 41002	2A2	M122439_009	not listed	zinc oxide silica mica
Coco Island SPF 30+ Broad Spectrum 4 Hours Water resistant WHITE ZINC CREAM 50 g Aust. L 162944	848WI	M122439_010	4	zinc oxide (320 mg/g)

Information on particle coating was not provided with the samples. It is likely that if the particles were coated, the coating would not be detectable by XRD due to the low relative concentrations involved, the nature of the coating (organic vs. inorganic) or the fact that the coating may be made of an amorphous material.

Samples M122439_007 and M122439_009 were not measured as they were duplicates of samples M122439_006 and M122439_008, respectively, and were provided in the event that there was insufficient material for extraction in one product tube.

In addition to the client's samples, XRD analysis of the following samples was performed as an internal reference:

- NIST SRM 1898, Titanium Dioxide Nanomaterial[3];
- Titanium (IV) oxide, rutile, powder, < 5 µm, ≥ 99.9 % metals basis (Aldrich, batch# 04410AJ);
- Titanium (IV) oxide, anatase, powder, < 5 µm, 98 % trace metals basis (Aldrich, batch# MKBK2645V);
- MKN-TiO2-R050P, Titanium oxide rutile nanopowder, TiO2-Rutile, 99 % pure, APS: 50 nm (MKnano, MKImpex, Canada, Lot# D0729);
- MKN-TiO2-A050, Titanium oxide rutile nanopowder, TiO2-Anatase, 98 % pure, APS: 50 nm (MKnano, MKImpex, Canada, Lot# D0711).

[3] SRM 1898 is certified for Brunauer-Emmet-Teller (BET) specific surface area, but has 'information values' for XRD measurements. It consists of anatase and rutile phases with relative fractions 0.76 ± 0.03 to 0.24 ± 0.03, respectively.

3. Summary of results

Figure 1 below shows the XRD data for all eight samples, as well as the five reference TiO_2 samples. The phase analysis of this data is summarised in Table 2.

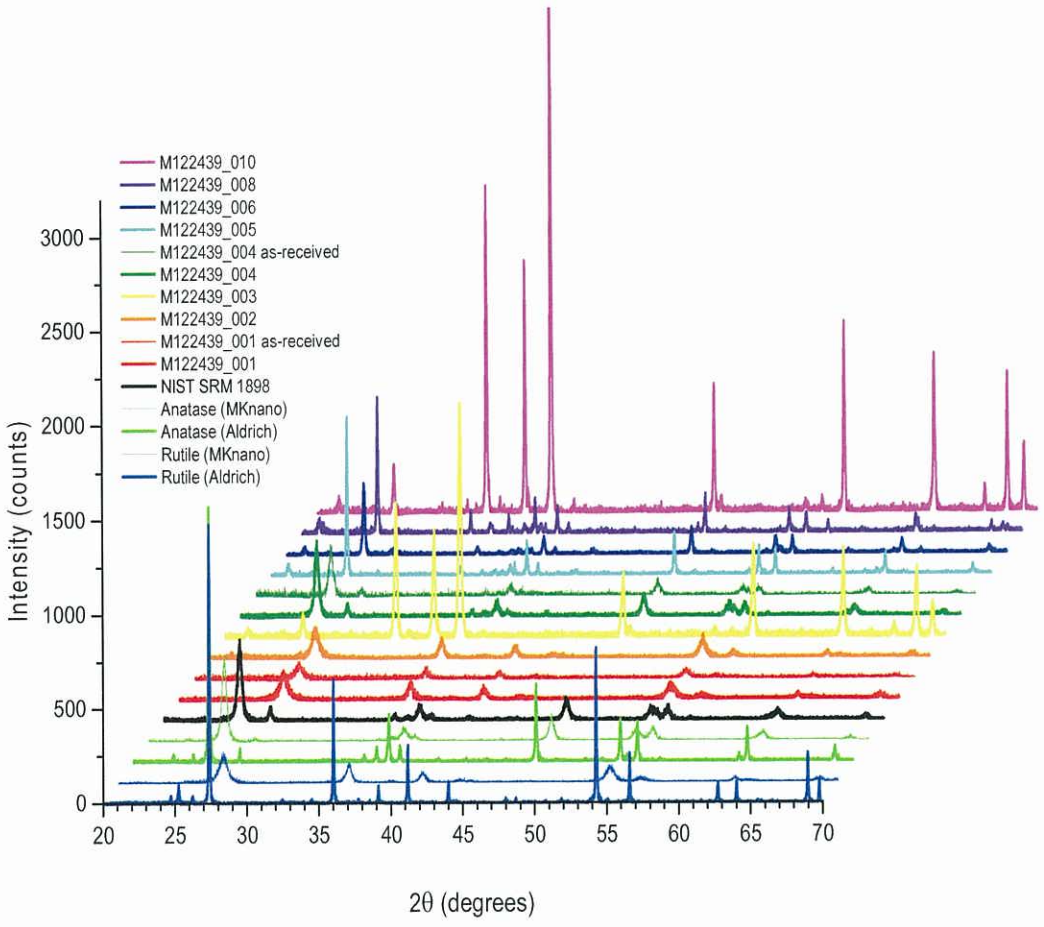


Figure 1: Overview of powder XRD data taken from the client's and reference samples.

Table 2 : Summary of phase analysis for the eight samples measured. Dominant TiO_2 phase indicated in bold typeface.

Sample reference number	Primary TiO_2 phase detected	Secondary TiO_2 phase detected	Other phases present
M122439_001	**rutile**	below detection threshold	below detection threshold
M122439_002	**rutile**	below detection threshold	below detection threshold
M122439_003	anatase	below detection threshold	**zincite** other unidentified phases
M122439_004	**anatase**	rutile	below detection threshold
M122439_005	**anatase**	rutile	haematite goethite
M122439_006	**anatase**	rutile	haematite goethite
M122439_008	**anatase**	below detection threshold	zincite other unidentified phases
M122439_010	anatase	below detection threshold	**zincite** other unidentified phases

4. Experimental details

XRD measurements were performed primarily on powders extracted from the sunscreens. XRD measurements of the as-received sunscreen were made on samples M122439_001 and M122439_004, as these contained the highest nominal mass fraction of TiO_2. Whilst it was possible to detect the TiO_2 present *in situ* in the as-received sunscreen, scattering from the formulation and the low TiO_2 mass fraction resulted in XRD spectra with low signal-to-noise ratios in which some of the minor diffraction peaks were obscured. In order to elucidate the composition of the solid fraction contained in the sunscreens more comprehensively, especially in the case of formulations with lower mass fractions of TiO_2, it was necessary to extract the solid fraction from the formulation.

The measurements on the sunscreen formulation are provided here for comparison and to demonstrate that the extraction process did not change the measured phase composition of the formulation.

4.1. Centrifugal extraction

To extract the inorganic (or solid) fraction present in the sunscreen formulation, the following procedure was applied. Steps 1–10 were performed on two separate aliquots of sunscreen formulation. The solid fraction of the aliquots remaining after step 11 was collated and dried to form the sample used for XRD analysis.

1. ~5 g of sunscreen was added to a 50 mL centrifuge tube (Nalgene, polypropylene copolymer).
2. Hexane (Sigma Aldrich, Chromasolv for HPLC ≥ 97.0 %, Lot# SZBC085CV) was added to the centrifuge tube to make up a total mass (tube + sunscreen + hexane) of 25 g.
3. The tube was capped, and vigorously shaken.
4. The tube was then vortexed (30 s) and ultrasonicated in a water bath (1 min).
5. The tube was placed in a centrifuge (Sigma 2-16P, rotor: 12151) and centrifuged at 7 000 rpm (5 205 g) for 30 mins.
6. Following centrifugation, the liquid in the tube was decanted, and the solid sediment fraction retained in the tube.
7. Methanol (Sigma Aldrich, Chromasolv for HPLC ≥ 99.9 %, Lot# SZBB111SV) was then added to the centrifuge tube to make up a total mass (tube + sunscreen + methanol) of 25 g.
8. Steps 3–6 were repeated.

9. Ultrapure de-ionised water (MilliQ, 18.2 MΩ cm) was then added to the centrifuge tube to make up a total mass (tube + sunscreen + water) of 30 g.
10. Steps 3–6 were repeated.
11. The solid fraction was then removed from the tube and placed on a watch-glass.
12. The watch-glass containing the solid fraction was placed in a laboratory oven (Labec) set to a temperature of 105 °C, and the sample was left to dry for at least 3 h.
13. Following drying, the sample was collected from the watch-glass and stored in a clean glass vial.

4.2. X-ray diffraction

XRD measurements were conducted on a PANalytical X'Pert PRO (Philips) X-ray diffractometer using Cu-K_α radiation (45 kV, 30 mA). Powder or sunscreen samples were applied to a holder puck with a shallow depression and flattened to be level with the top surface of the puck. The sample puck was rotated with a revolution time of 2 s during measurement. Diffraction patterns were collected over the angular range 2θ = 20–70 ° with Data Collector Software (PANalytical, Philips, v. 4.1.0.25). The angular step size was 0.005 ° with a dwell time per step of 1 s.

After analysis, the raw data was transferred to HighScore Plus software (PANalytical, Philips, v. 3.0e), and an automatic algorithm was applied to remove the background signal, strip the Cu-$K_{\alpha 2}$ X-ray line from the data, and to detect the peaks present in the measured data. Peak positions were compared to the internal references and to reference XRD spectra available on the International Centre for Diffraction Data's Joint Committee on Powder Diffraction Standards (JCPDS) database[4] for pattern matching/phase identification (see Appendix A for JCPDS data file information).

5. Results

5.1. M122439_001

XRD spectra recorded for samples M122439_001 are given in Figure 2 and Figure 3. Figure 2 shows the spectrum of the as-received sunscreen, and Figure 3 shows the spectrum from the solid fraction extracted from the sunscreen. The high background signal and reduced peak intensities observed in Figure 2 are indications of diffuse scattering from the formulation. As a consequence, some of the diffraction peaks expected for TiO_2 (in this case, the rutile phase)

[4] http://www.icdd.com/, October 2012.

are obscured by the background. However, excellent correlation can still be observed between the features in Figure 2 and Figure 3, demonstrating that the extraction process has not altered the phase composition of the solid fraction present in the sunscreen.

Pattern matching of the XRD spectra indicates that the only crystalline phase present in this sample is rutile TiO_2 (reference spectrum 21-1276 from the JCPDS database).

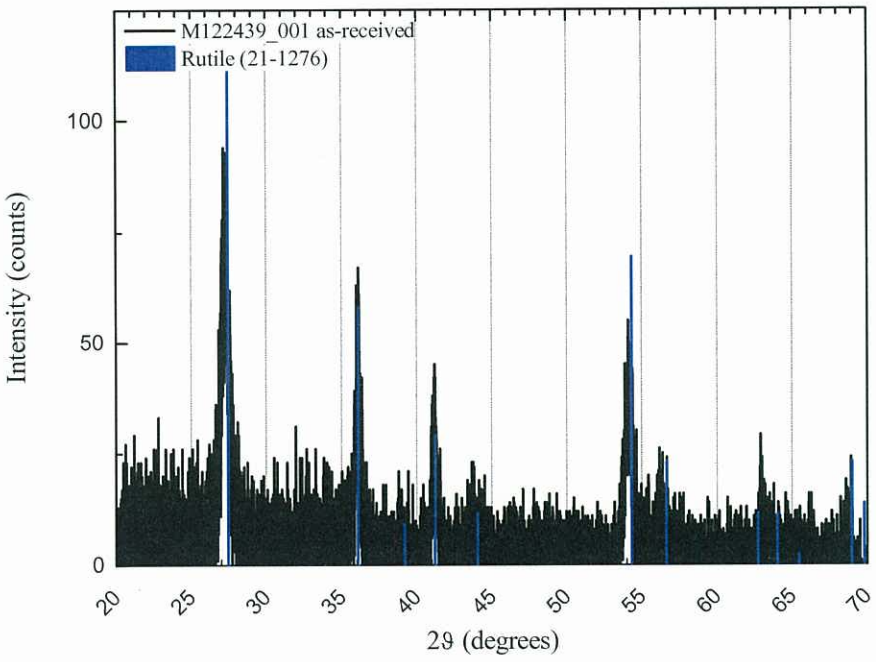


Figure 2: XRD spectrum of as-received sample M122439_001, with reference peak positions of rutile (JCPDS database entry number 21-1276).

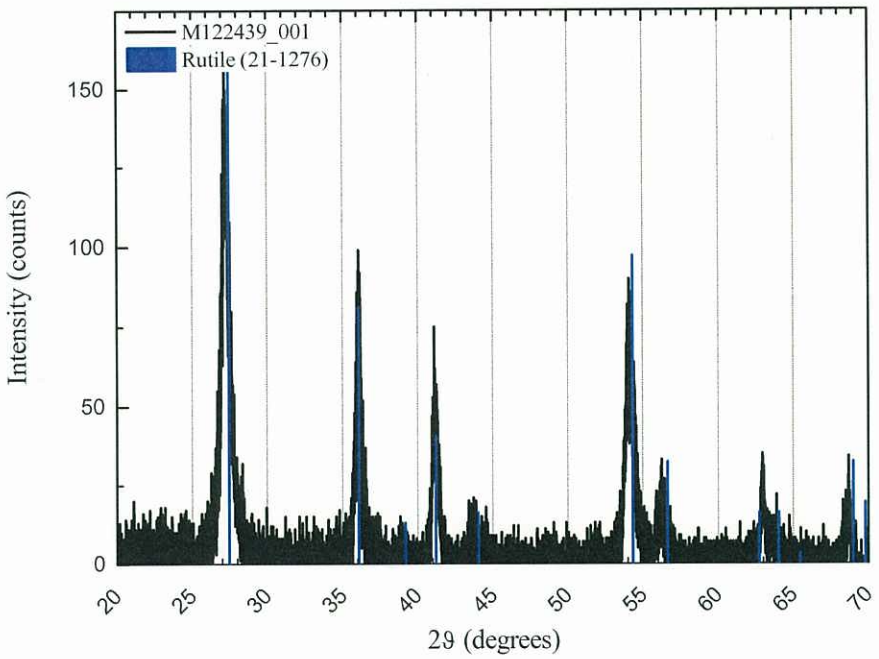


Figure 3: XRD spectrum of powder extracted from sample M122439_001, with reference peak positions of rutile (JCPDS database entry number 21-1276).

5.2 M122439_002

The XRD spectrum recorded for sample M122439_002 is given in Figure 4. Pattern matching of this spectrum indicates that the only crystalline phase present in this sample is rutile TiO_2 (reference spectrum 21-1276 from the JCPDS database).

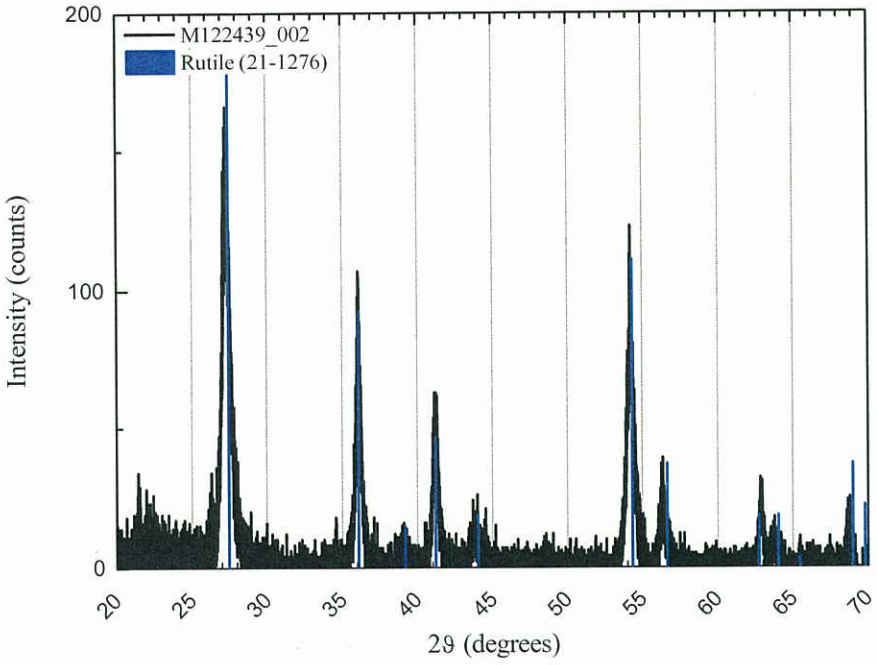


Figure 4: XRD spectrum of powder extracted from sample M122439_002, with reference peak positions of rutile (JCPDS database entry number 21-1276).

5.3 M122439_003

The XRD spectrum recorded for sample M122439_003 is given in Figure 5. Sample M122439_003 contained nominally 320 mg/g ZnO, and the characteristic zincite ZnO peaks are clearly seen in this spectrum as the dominant features (strongest lines at 2θ = 32 °, 34 ° and 36 °, JCPDS entry 70-2551, see Appendix A). Pattern matching of this spectrum indicates that the only crystalline phase of TiO_2 present in this sample is anatase TiO_2 (reference spectrum 21-1272 from the JCPDS database). The weak spectral feature at ~21 ° cannot be attributed to zincite ZnO or anatase TiO_2, and may be associated with a silica-based crystalline substance present in the formulation.

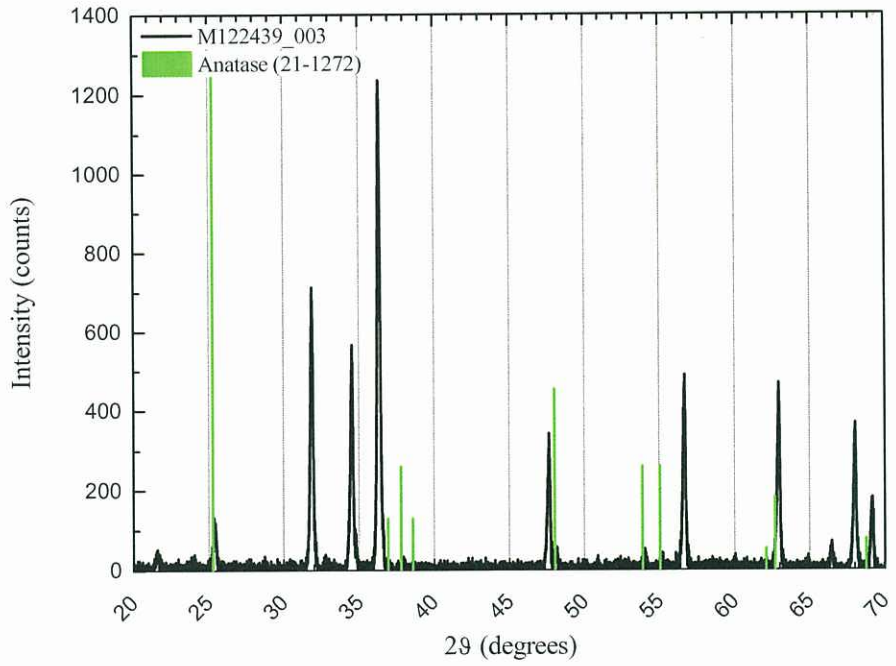


Figure 5: XRD spectrum of powder extracted from sample M122439_003, with reference peak positions of anatase (JCPDS database entry number 21-1272).

5.4 M122439_004

XRD spectra recorded for samples M122439_004 are given in Figure 6 and Figure 7. Figure 6 shows the spectrum of the as-received sunscreen, and Figure 7 shows the spectrum of the solid fraction extracted from the sunscreen. The high background signal and reduced intensities present in Figure 6 are indications of diffuse scattering from the formulation. As a consequence, some of the diffraction peaks expected for TiO_2 (in this case, the rutile phase) are obscured by the background.. However, as with sample M122439_001, excellent correlation can still be observed between the spectral features in Figure 6 and Figure 7, demonstrating that the extraction process has not altered the phase composition of the solid fraction present in the sunscreen.

Pattern matching of the XRD spectra indicates that both anatase and rutile TiO_2 crystal phases are present in this sample (reference spectra 21-1272 and 21-1276, respectively, from the JCPDS database). The anatase phase is present in higher proportions than the rutile phase.

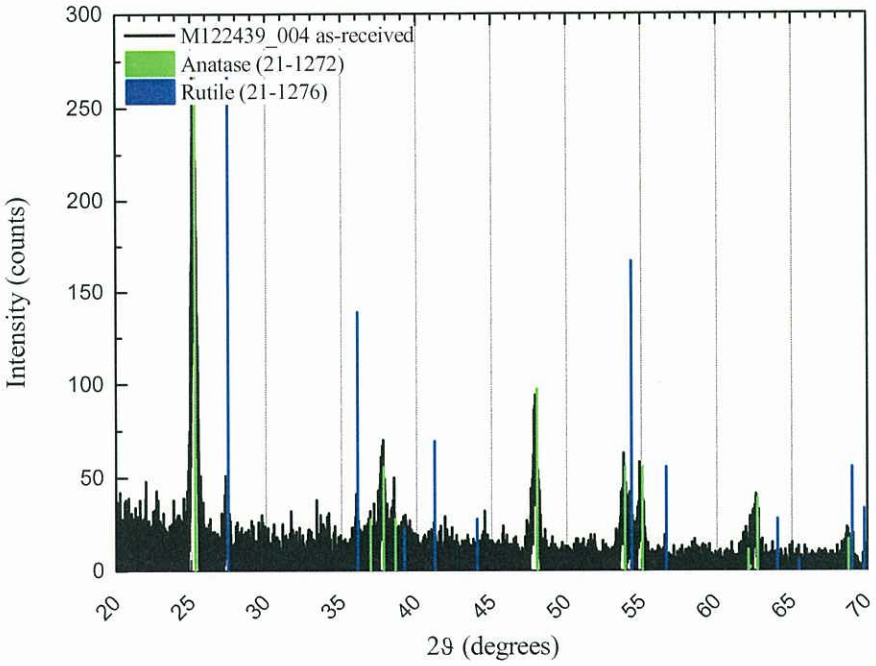


Figure 6: XRD spectrum of as-received sample M122439_004, with reference peak positions of anatase and rutile (JCPDS database entry numbers 21-1272 and 21-1276, respectively).

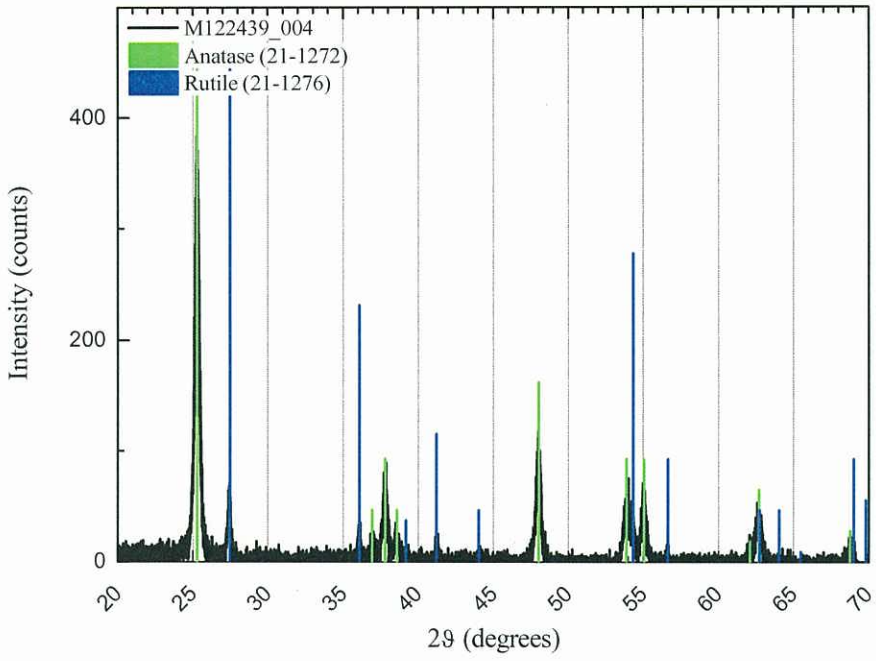


Figure 7: XRD spectrum of powder extracted from sample M122439_004, with reference peak positions of anatase and rutile (JCPDS database entry numbers 21-1272 and 21-1276, respectively).

5.5 M133439_005

The XRD spectrum recorded for sample M122439_005 is given in Figure 8. Sample M122439_005 is labelled as containing iron oxides in addition to TiO_2. XRD peaks associated with anatase and rutile TiO_2 phases (reference spectra 21-1272 and 21-1276 from the JCPDS database) can be identified. Features relating to haematite and goethite can also be identified (Fe_2O_3, JCPDS entry 89-0598, and FeO(OH), JCPDS entry 81-0463, respectively; see Appendix A). Anatase is the dominant phase present.

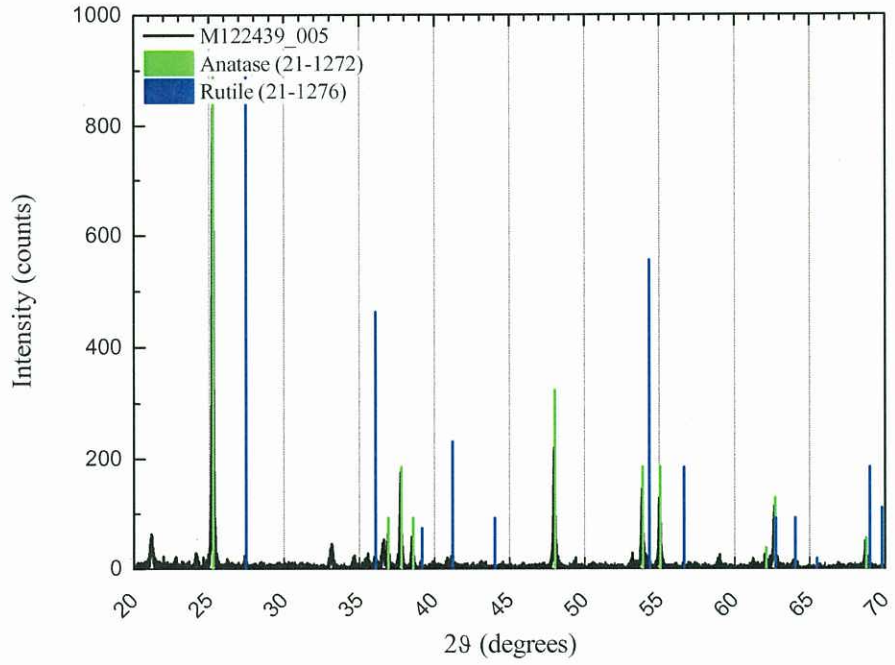


Figure 8: XRD spectrum of powder extracted from sample M122439_005, with reference peak positions of anatase and rutile (JCPDS database entry numbers 21-1272 and 21-1276, respectively).

5.6 M122439_006

The XRD spectrum recorded for sample M122439_006 is given in Figure 9. Sample M122439_006 is labelled as containing talc and iron oxides in addition to TiO_2. XRD peaks associated with anatase and rutile TiO_2 phases (reference spectra 21-1272 and 21-1276 from the JCPDS database) can be identified. Features relating to haematite and goethite can also be identified (Fe_2O_3, JCPDS entry 89-0598, and FeO(OH), JCPDS entry 81-0463, respectively; see Appendix A). Anatase is the dominant phase present.

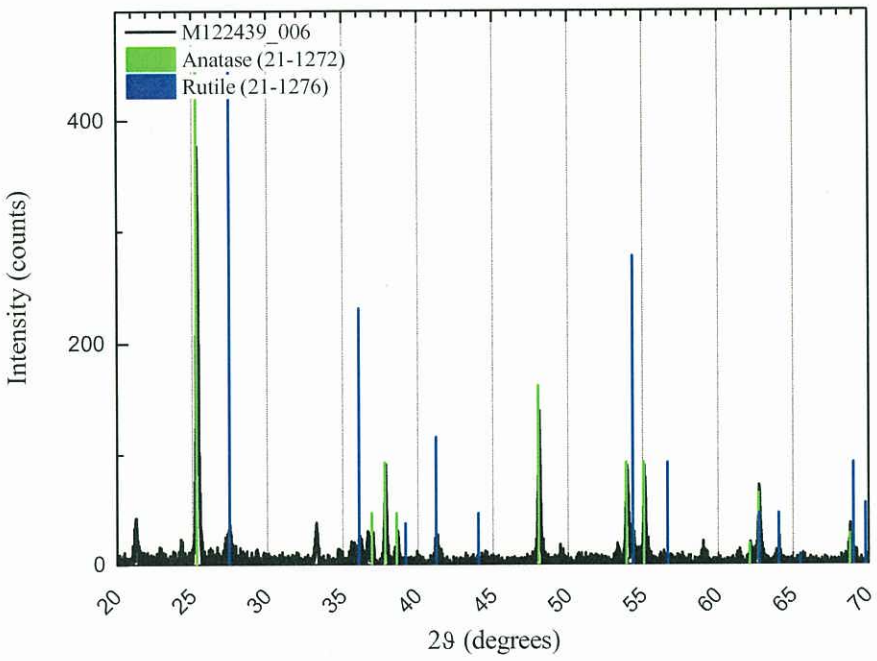


Figure 9: XRD spectrum of powder extracted from sample M122439_006, with reference peak positions of anatase and rutile (JCPDS database entry numbers 21-1272 and 21-1276, respectively).

5.7 M122439_008

The XRD spectrum recorded for sample M122439_008 is given in Figure 10. Sample M122439_008 is labelled as containing zinc oxide, silica and mica in addition to TiO_2. XRD peaks associated with the anatase TiO_2 phase (reference spectra 21-1272 from the JCPDS database) were identified, as well as features relating to zincite ZnO (JCPDS entry 70-2551, see Appendix A). Due to the numerous possible crystalline phases of mica (minerals based on silicates) and silica, it was not possible to completely identify all phases present in this sample. Anatase TiO_2 is the dominant phase present.

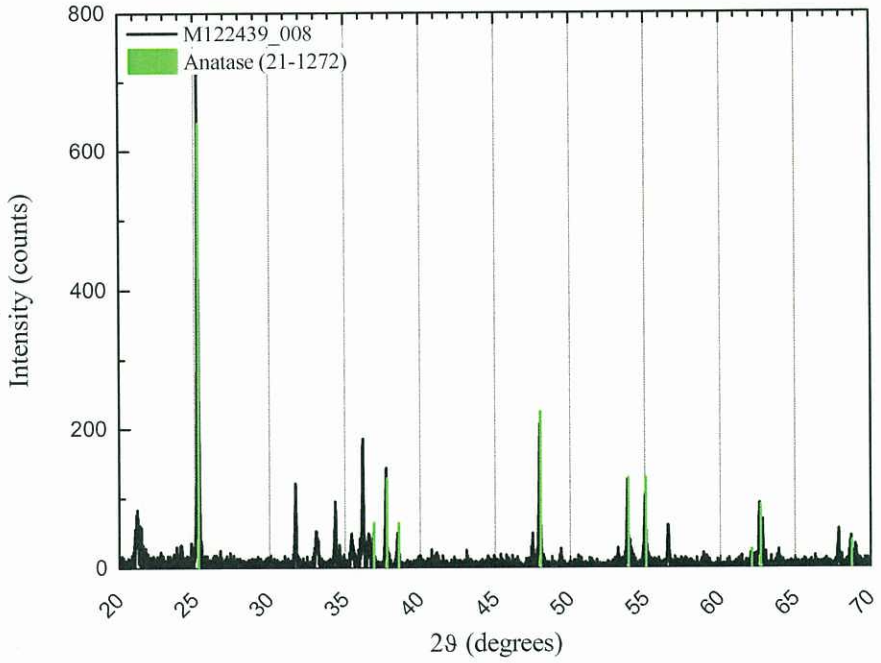


Figure 10: XRD spectrum of powder extracted from sample M122439_008, with reference peak positions of anatase (JCPDS database entry number 21-1272).

5.8 M122439_010

The XRD spectrum recorded for sample M122439_010 is given in Figure 11. Sample M122439_010 contained 320 mg/g ZnO, and the characteristic zincite ZnO peaks are clearly recognisable in this spectrum as the dominant features (strongest lines at 2θ = 32 °, 34 ° and 36 °, JCPDS entry 70-2551, see Appendix A). Pattern matching of this spectrum indicates that the only crystalline phase of TiO_2 present in this sample is anatase TiO_2 (reference spectrum 21-1272 from the JCPDS database). The weak spectral feature at ~ 21 ° cannot be attributed to zincite ZnO or anatase TiO_2, and may be associated with a silica-based crystalline substance present in the formulation.

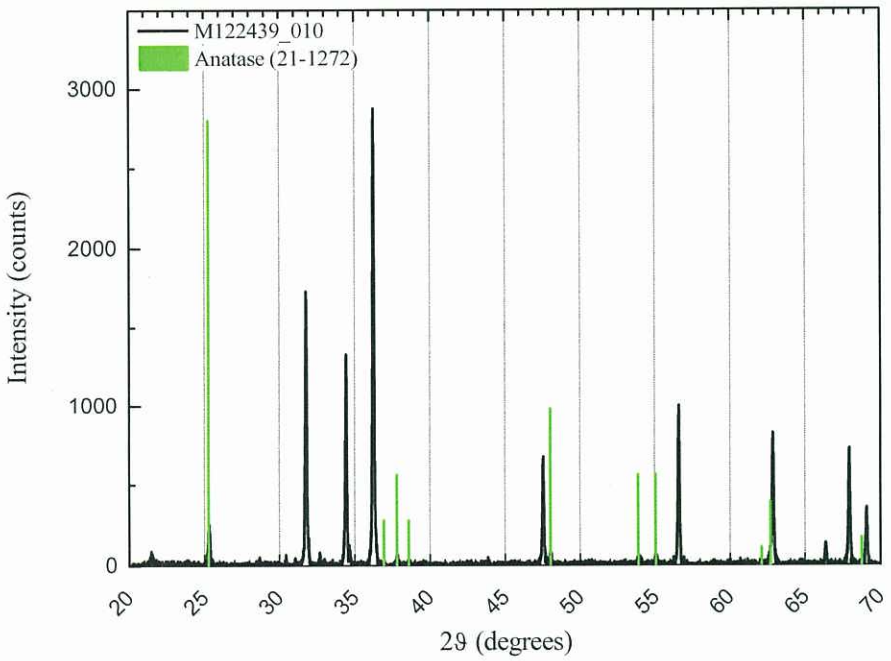


Figure 11: XRD spectrum of powder extracted from sample M122439_010, with reference peak positions of anatase (JCPDS database entry number 21-1272).

7. Conclusion

Of the eight sunscreens tested, three contained anatase, three contained a blend of anatase and rutile with anatase present in higher proportion than rutile, and two contained rutile only (within the detection limits of the method).

Acknowledgements

NMI acknowledges CSIRO Material Sciences and Engineering for access to the XRD instrument.

Appendix A JCPDS database phase information

Anatase (TiO_2)

Name and formula

Reference code:	00-021-1272
Mineral name:	Anatase, syn
Compound name:	Titanium Oxide
PDF index name:	Titanium Oxide
Empirical formula:	O_2Ti
Chemical formula:	TiO_2

Crystallographic parameters

Crystal system:	Tetragonal
Space group:	I41/amd
Space group number:	141
a (Å):	3.7852
b (Å):	3.7852
c (Å):	9.5139
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	90.0000
Calculated density (g/cm^3):	3.89
Volume of cell (10^6 pm^3):	136.31
Z:	4.00
RIR:	3.30

Subfiles and quality

Subfiles:	Alloy, metal or intermetalic Common Phase Corrosion Educational pattern Excipient Forensic Inorganic Mineral NBS pattern Pharmaceutical Pigment/Dye
Quality:	Star (S)

Comments

Color:	Colorless
Creation Date:	1/01/1970
Modification Date:	24/01/2006
General Comments:	Pattern reviewed by Holzer, J., McCarthy, G., North Dakota State Univ, Fargo, North Dakota, USA, ICDD Grant-in-Aid (1990). Agrees well with experimental and calculated patterns
Additional Patterns:	See PDF 01-071-1166. Validated by calculated pattern
Color:	Colorless
Polymorphism/Phase Transition:	Anatase and another polymorph, brookite (orthorhombic), are converted to rutile (tetragonal) by heating above 700 C
Sample Source or Locality:	Sample obtained from National Lead Co., South Amboy, New Jersey, USA
Temperature of Data Collection:	Pattern taken at 298 K
Unit Cell Data Source:	Powder Diffraction.

References

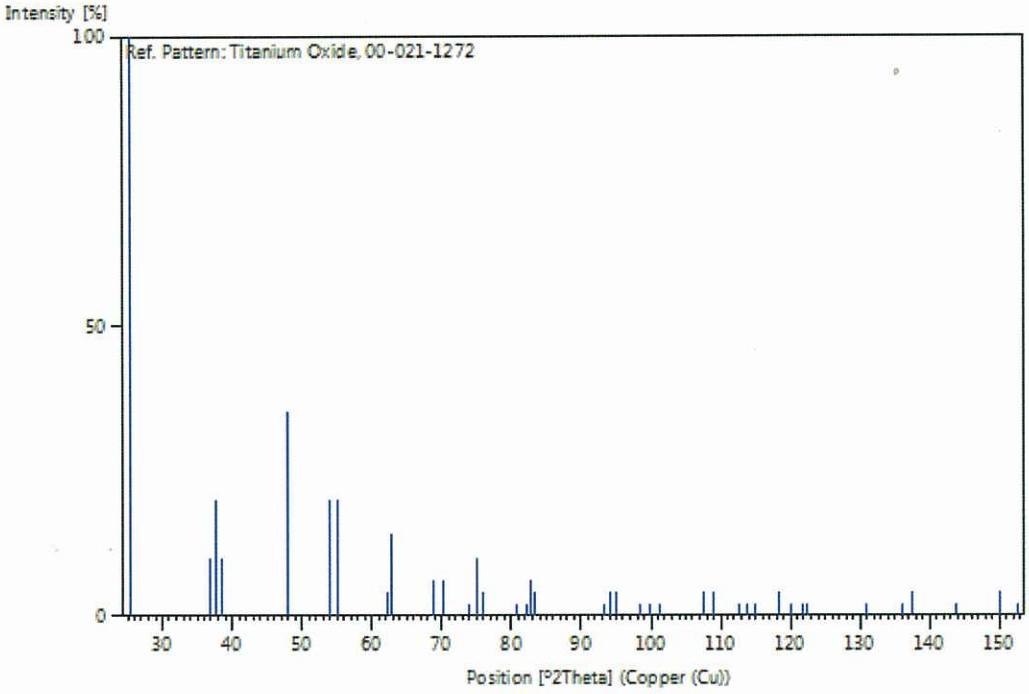
Primary reference: *Natl. Bur. Stand. (U.S.) Monogr. 25*, **7**, 82, (1969)

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	0	1	3.52000	25.281	100.0
2	1	0	3	2.43100	36.947	10.0
3	0	0	4	2.37800	37.801	20.0
4	1	1	2	2.33200	38.576	10.0
5	2	0	0	1.89200	48.050	35.0
6	1	0	5	1.69990	53.891	20.0
7	2	1	1	1.66650	55.062	20.0
8	2	1	3	1.49300	62.121	4.0
9	2	0	4	1.48080	62.690	14.0
10	1	1	6	1.36410	68.762	6.0
11	2	2	0	1.33780	70.311	6.0
12	1	0	7	1.27950	74.031	2.0
13	2	1	5	1.26490	75.032	10.0
14	3	0	1	1.25090	76.020	4.0
15	0	0	8	1.18940	80.727	2.0
16	3	0	3	1.17250	82.139	2.0
17	2	2	4	1.16640	82.662	6.0
18	3	1	2	1.16080	83.149	4.0
19	2	1	7	1.06000	93.221	2.0
20	3	0	5	1.05170	94.182	4.0
21	3	2	1	1.04360	95.143	4.0
22	1	0	9	1.01820	98.319	2.0
23	2	0	8	1.00700	99.804	2.0
24	3	2	3	0.99670	101.221	2.0
25	3	1	6	0.95550	107.448	4.0
26	4	0	0	0.94640	108.963	4.0
27	3	0	7	0.92460	112.841	2.0
28	3	2	5	0.91920	113.861	2.0
29	4	1	1	0.91380	114.909	2.0
30	2	1	9	0.89660	118.439	4.0
31	2	2	8	0.88900	120.104	2.0
32	4	1	3	0.88190	121.725	2.0
33	4	0	4	0.87930	122.336	2.0
34	4	2	0	0.84640	131.036	2.0
35	3	2	7	0.83080	135.998	2.0
36	4	1	5	0.82680	137.391	4.0

37	3	0	9	0.81020	143.888	2.0
38	4	2	4	0.79740	150.039	4.0
39	0	0	12	0.79280	152.634	2.0

Stick Pattern



Rutile (TiO_2)

Name and formula

Reference code:	00-021-1276
Mineral name:	Rutile, syn
Compound name:	Titanium Oxide
Common name:	titania
PDF index name:	Titanium Oxide
Empirical formula:	O_2Ti
Chemical formula:	TiO_2

Crystallographic parameters

Crystal system:	Tetragonal
Space group:	P42/mnm
Space group number:	136
a (Å):	4.5933
b (Å):	4.5933
c (Å):	2.9592

Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	90.0000
Calculated density (g/cm^3):	4.25
Measured density (g/cm^3):	4.23
Volume of cell (10^6 pm^3):	62.43
Z:	2.00
RIR:	3.40

Subfiles and quality

Subfiles:	Alloy, metal or intermetalic Common Phase Corrosion Educational pattern Excipient Forensic Inorganic Mineral NBS pattern Pharmaceutical Pigment/Dye
Quality:	Star (S)

Comments

Color:	White
Creation Date:	1/01/1970
Modification Date:	24/01/2006
General Comments:	Pattern reviewed by Syvinski, W., McCarthy, G., North Dakota State Univ, Fargo, North Dakota, USA, ICDD Grant-in-Aid (1990). Agrees well with experimental and calculated patterns. Additional weak reflections (indicated by brackets) were observed. Naturally occurring material may be reddish brown
Additional Patterns:	Validated by calculated pattern
Analysis:	No impurity over 0.001%
Color:	White
Polymorphism/Phase Transition:	Two other polymorphs, anatase (tetragonal) and brookite (orthorhombic), converted to rutile on heating above 700 C
Reflectance:	Opaque mineral optical data on specimen from Sweden: R3R%=20.3, Disp.=Std. Sample Source or Locality: Sample obtained from National Lead Co., South Amboy, New Jersey, USA. Temperature of Data Collection: Pattern taken at 298 K. Vickers Hardness Number: VHN100=1132-1187. Unit Cell Data Source: Powder Diffraction.

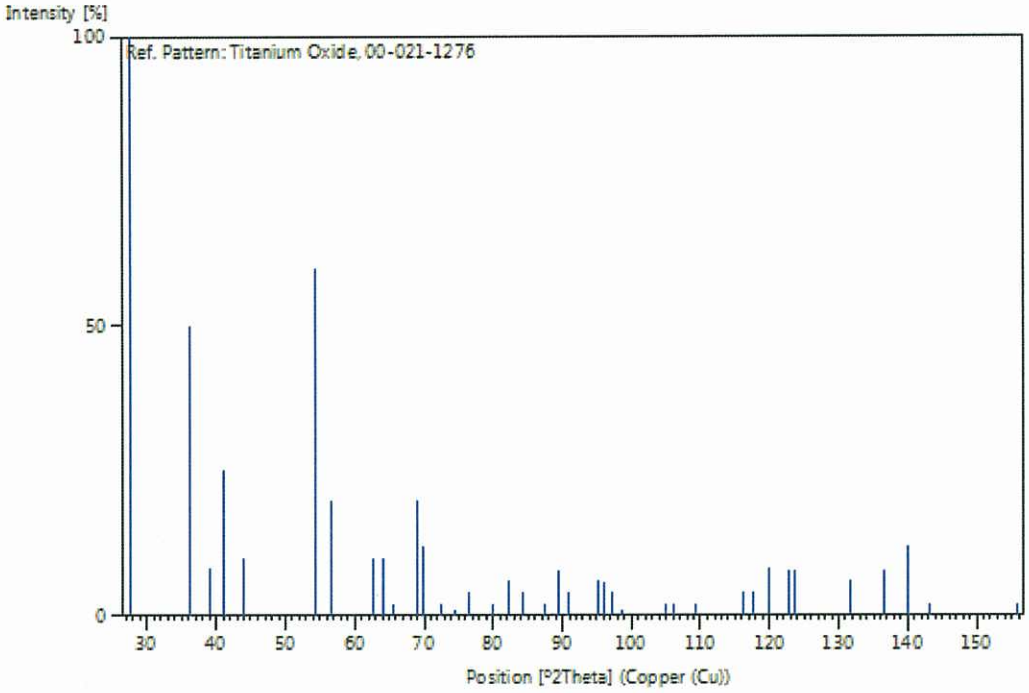
References

Primary reference:	*Natl. Bur. Stand. (U.S.) Monogr. 25*, **7**, 83, (1969)
Optical data:	*Dana's System of Mineralogy, 7th Ed.*, **I**, 575

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	1	0	3.24700	27.447	100.0
2	1	0	1	2.48700	36.086	50.0
3	2	0	0	2.29700	39.188	8.0
4	1	1	1	2.18800	41.226	25.0
5	2	1	0	2.05400	44.052	10.0
6	2	1	1	1.68740	54.323	60.0
7	2	2	0	1.62370	56.642	20.0
8	0	0	2	1.47970	62.742	10.0
9	3	1	0	1.45280	64.040	10.0
10	2	2	1	1.42430	65.480	2.0
11	3	0	1	1.35980	69.010	20.0
12	1	1	2	1.34650	69.790	12.0
13	3	1	1	1.30410	72.410	2.0
14	3	2	0	1.27390	74.411	1.0
15	2	0	2	1.24410	76.510	4.0
16	2	1	2	1.20060	79.822	2.0
17	3	2	1	1.17020	82.335	6.0
18	4	0	0	1.14830	84.260	4.0
19	4	1	0	1.11430	87.464	2.0
20	2	2	2	1.09360	89.557	8.0
21	3	3	0	1.08270	90.708	4.0
22	4	1	1	1.04250	95.275	6.0
23	3	1	2	1.03640	96.017	6.0
24	4	2	0	1.02710	97.177	4.0
25	3	3	1	1.01670	98.514	1.0
26	4	2	1	0.97030	105.099	2.0
27	1	0	3	0.96440	106.019	2.0
28	1	1	3	0.94380	109.406	2.0
29	4	0	2	0.90720	116.227	4.0
30	5	1	0	0.90090	117.527	4.0
31	2	1	3	0.88920	120.059	8.0
32	4	3	1	0.87740	122.788	8.0
33	3	3	2	0.87380	123.660	8.0
34	4	2	2	0.84370	131.847	6.0
35	3	0	3	0.82920	136.549	8.0
36	5	2	1	0.81960	140.052	12.0
37	4	4	0	0.81200	143.116	2.0
38	5	3	0	0.78770	155.870	2.0

Stick Pattern



Zincite (ZnO)

Name and formula

Reference code:	01-070-2551
Mineral name:	Zincite, syn
Compound name:	Zinc Oxide
PDF index name:	Zinc Oxide
Empirical formula:	OZn
Chemical formula:	ZnO

Crystallographic parameters

Crystal system:	Hexagonal
Space group:	P63mc
Space group number:	186
a (Å):	3.2490
b (Å):	3.2490
c (Å):	5.2070
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	120.0000
Calculated density (g/cm^3):	5.68
Volume of cell (10^6 pm^3):	47.60
Z:	2.00

RIR: 5.87

Subfiles and quality

Subfiles: Alloy, metal or intermetalic
Corrosion
ICSD Pattern
Inorganic
Mineral
Quality: Blank (B)

Comments

ANX: NO
ICSD collection code: 41488
Creation Date: 27/06/2003
Modification Date: 25/01/2006
Additional Patterns: See PDF 01-089-0510 and PDF 01-079-2205
ANX: NO
ICSD Collection Code: 41488
Calculated Pattern Original Remarks: REM M Wurtzite-type, cp. 34477. REM M PDF 00-036-1451
Test from ICSD: REF Physical Review, Serie 3. B - Condensed Matter (18,. CLAS 6mm (Hermann-Mauguin) - C6v (Schoenflies). PRS hP4. No R value given in the paper. (Code 51). At least one temperature factor missing in the paper. (C
Minor Warning: No R value given in the paper. No e.s.d. reported/abstracted on the cell dimension
Significant Warning: ICSD Warning: The coordinates are those given in the paper but the atomic distances do not agree with those calculated during testing.The coordinates are probably correct. Wyckoff Sequence: b2 (P63MC).

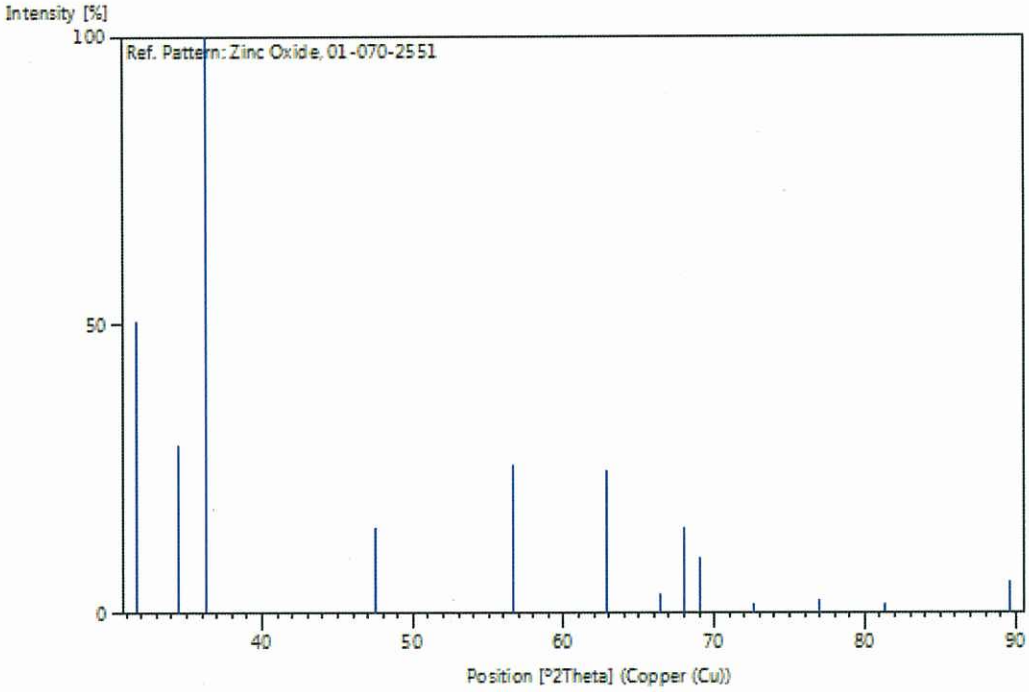
References

Primary reference: *Calculated from ICSD using POWD-12++*
Structure: Xu, Y.-N., Ching, W.Y., *Phys. Rev. B: Condens. Matter. Mater. Phys.*, **48**, 4335, (1993)

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	0	0	2.81372	31.777	50.7
2	0	0	2	2.60350	34.420	29.4
3	1	0	1	2.47542	36.261	100.0
4	1	0	2	1.91095	47.544	14.9
5	1	1	0	1.62450	56.612	25.8
6	1	0	3	1.47722	62.859	24.9
7	2	0	0	1.40686	66.396	3.3
8	1	1	2	1.37821	67.961	14.8
9	2	0	1	1.35816	69.105	9.4
10	0	0	4	1.30175	72.561	1.6
11	2	0	2	1.23771	76.977	2.2
12	1	0	4	1.18144	81.385	1.5
13	2	0	3	1.09292	89.628	5.7

Stick Pattern



Hematite (Fe_2O_3)

Name and formula

Reference code:	01-089-0598
Mineral name:	Hematite, syn
Compound name:	Iron Oxide
Common name:	α-Fe2 O3, iron(III) oxide
PDF index name:	Iron Oxide
Empirical formula:	Fe_2O_3
Chemical formula:	Fe_2O_3

Crystallographic parameters

Crystal system:	Rhombohedral
Space group:	R-3c
Space group number:	167
a (Å):	5.0380
b (Å):	5.0380
c (Å):	13.7760
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	120.0000

Calculated density (g/cm^3):	5.25
Volume of cell (10^6 pm^3):	302.81
Z:	6.00
RIR:	3.20

Subfiles and quality

Subfiles:	Alloy, metal or intermetalic Corrosion Excipient ICSD Pattern Inorganic Mineral Pharmaceutical
Quality:	Star (S)

Comments

ANX:	A2X3
ICSD collection code:	82136
Creation Date:	6/07/2000
Modification Date:	25/01/2006
Additional Patterns:	See PDF 01-089-2810
ANX:	A2X3
ICSD Collection Code:	82136
Calculated Pattern Original Remarks:	Sample mechanically activated in a ball mill under Aratmosphere for 15 min and than annealed in air at 673 K. X-ray diffraction (powder)
Temperature Factor:	ITF
Wyckoff Sequence:	e c (R3-CH)
Unit Cell Data Source:	Powder Diffraction.

References

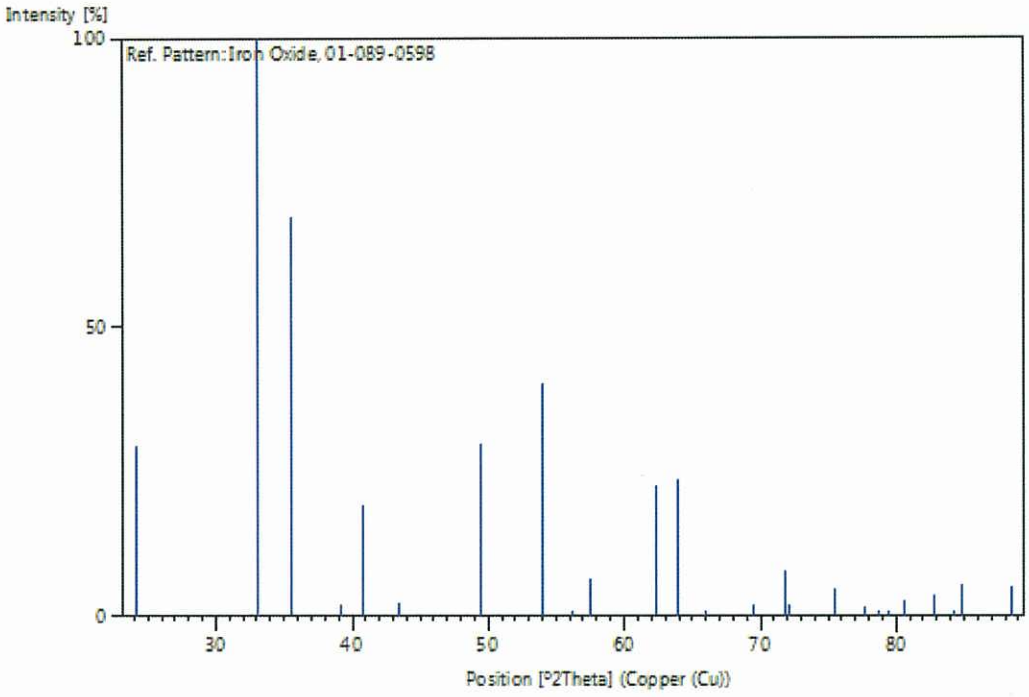
Primary reference:	*Calculated from ICSD using POWD-12++*
Structure:	Sadykov, V.A., Isupova, L.A., Tsybulya, S.V., Cherepanova, S.V., Litvak, G.S., Burgina, E.B., Kustova, G.N., Kolomiichuk, V.N., Ivanov, V.P., Paukshtis, E.A., Golovin, A.V., Avvakumov, E.G., *J. Solid State Chem.*, **123**, 191, (1996)

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	0	1	2	3.68582	24.126	29.7
2	1	0	4	2.70329	33.112	100.0
3	1	1	0	2.51900	35.612	69.0
4	0	0	6	2.29600	39.205	2.2
5	1	1	3	2.20853	40.826	19.1
6	2	0	2	2.07971	43.479	2.5
7	0	2	4	1.84291	49.414	29.8
8	1	1	6	1.69689	53.995	40.3
9	2	1	1	1.63738	56.127	0.2
10	0	1	8	1.60176	57.490	6.4
11	1	2	2	1.60176	57.490	6.4

12	2	1	4	1.48736	62.383	22.5
13	3	0	0	1.45435	63.964	23.5
14	1	2	5	1.41498	65.966	0.1
15	2	0	8	1.35164	69.487	2.0
16	1	0	10	1.31367	71.800	7.8
17	1	1	9	1.30810	72.154	1.8
18	2	2	0	1.25950	75.409	4.6
19	0	3	6	1.22861	77.654	1.7
20	2	2	3	1.21464	78.718	0.9
21	1	3	1	1.20545	79.437	0.1
22	1	2	8	1.19102	80.595	2.8
23	3	1	2	1.19102	80.595	2.8
24	0	2	10	1.16479	82.801	3.9
25	0	0	12	1.14800	84.288	0.2
26	1	3	4	1.14167	84.864	5.6
27	2	2	6	1.10426	88.465	5.2

Stick Pattern



Goethite (FeO(OH))

Name and formula

Reference code:	01-081-0463
Mineral name:	Goethite, syn
Compound name:	Iron Oxide Hydroxide
PDF index name:	Iron Oxide Hydroxide
Empirical formula:	$FeHO_2$
Chemical formula:	FeO (OH)

Crystallographic parameters

Crystal system:	Orthorhombic
Space group:	Pbnm
Space group number:	62
a (Å):	4.6158
b (Å):	9.9545
c (Å):	3.0233
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	90.0000
Calculated density (g/cm^3):	4.25
Volume of cell (10^6 pm^3):	138.91
Z:	4.00
RIR:	2.79

Subfiles and quality

Subfiles:	Corrosion ICSD Pattern Inorganic Mineral
Quality:	Indexed (I)

Comments

ANX:	AX2
ICSD collection code:	71809
Creation Date:	15/12/1998
Modification Date:	25/01/2006
ANX:	AX2
ICSD Collection Code:	71809
Note:	Rietveld profile refinement applied
Calculated Pattern Original Remarks:	ATOM H 1 +1. 4.00 Atoms not located in unit cell
Test from ICSD:	At least one TF missing
Minor Warning:	No e.s.d. reported/abstracted on the cell dimension. Incomplete determination of H atom positions in the structure
Wyckoff Sequence:	c3 (PBNM)
Unit Cell Data Source:	Rietveld or profile fit analysis.

References

Primary reference:	*Calculated from ICSD using POWD-12++*, (1997)
Structure:	Hazemann, J.L., Berar, J.F., Manceau, A., *Materials Science Forum*, **79**, 821, (1991)

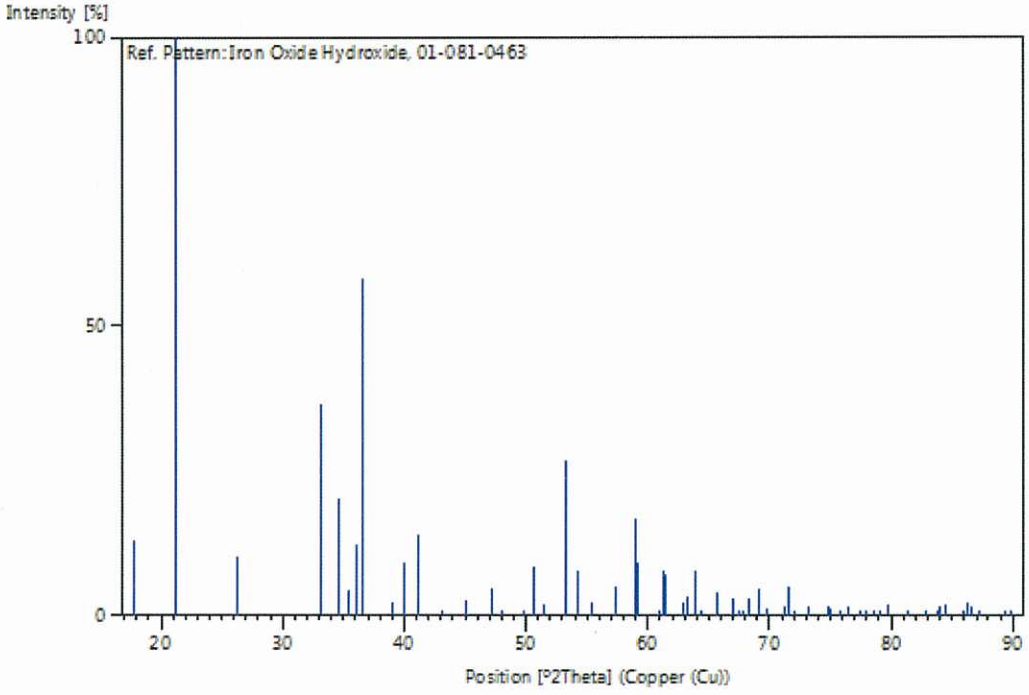
Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]

1	0	2	0	4.97725	17.806	13.1
2	1	1	0	4.18752	21.200	100.0
3	1	2	0	3.38444	26.312	10.3
4	1	3	0	2.69425	33.226	36.4
5	0	2	1	2.58396	34.688	20.4
6	1	0	1	2.52908	35.465	4.4
7	0	4	0	2.48862	36.062	12.5
8	1	1	1	2.45121	36.631	58.2
9	2	0	0	2.30790	38.995	2.4
10	1	2	1	2.25470	39.954	9.1
11	2	1	0	2.24827	40.073	7.1
12	1	4	0	2.19053	41.177	13.9
13	2	2	0	2.09376	43.173	1.0
14	1	3	1	2.01143	45.034	2.8
15	0	4	1	1.92140	47.270	4.7
16	2	3	0	1.89467	47.978	0.4
17	1	5	0	1.82810	49.842	0.7
18	2	1	1	1.80410	50.551	8.6
19	1	4	1	1.77386	51.475	2.0
20	2	2	1	1.72129	53.168	26.8
21	2	4	0	1.69222	54.156	7.6
22	0	6	0	1.65908	55.329	2.5
23	2	3	1	1.60546	57.345	5.2
24	1	5	1	1.56435	58.998	16.9
25	1	6	0	1.56129	59.125	9.2
26	3	1	0	1.52054	60.875	0.5
27	0	0	2	1.51165	61.271	7.7
28	2	5	0	1.50750	61.458	7.1
29	2	4	1	1.47664	62.887	2.3
30	3	2	0	1.46997	63.205	3.3
31	0	6	1	1.45447	63.958	7.7
32	0	2	2	1.44641	64.357	0.6
33	1	1	2	1.42184	65.607	4.1
34	3	3	0	1.39584	66.989	3.2
35	1	6	1	1.38723	67.460	0.1
36	1	2	2	1.38023	67.848	0.8
37	3	0	1	1.37124	68.354	2.9
38	3	1	1	1.35903	69.055	4.5
39	1	7	0	1.35903	69.055	4.5
40	2	6	0	1.34712	69.753	1.4
41	3	2	1	1.32199	71.279	1.5
42	1	3	2	1.31832	71.508	5.0
43	3	4	0	1.30868	72.117	0.1
44	0	4	2	1.29198	73.199	1.8
45	3	3	1	1.26729	74.866	1.5
46	2	0	2	1.26454	75.057	1.3
47	2	1	2	1.25446	75.766	0.5
48	1	4	2	1.24416	76.506	1.8
49	0	8	0	1.24416	76.506	1.8
50	2	6	1	1.23050	77.512	0.3
51	2	2	2	1.22561	77.880	0.2
52	3	5	0	1.21742	78.504	0.1
53	2	7	0	1.21069	79.025	0.1
54	3	4	1	1.20099	79.791	2.0
55	1	8	0	1.20099	79.791	2.0
56	2	3	2	1.18164	81.369	0.1
57	1	5	2	1.16496	82.787	0.1
58	4	0	0	1.15395	83.754	0.3
59	0	8	1	1.15067	84.047	1.5
60	4	1	0	1.14627	84.444	1.9
61	3	5	1	1.12930	86.017	0.8

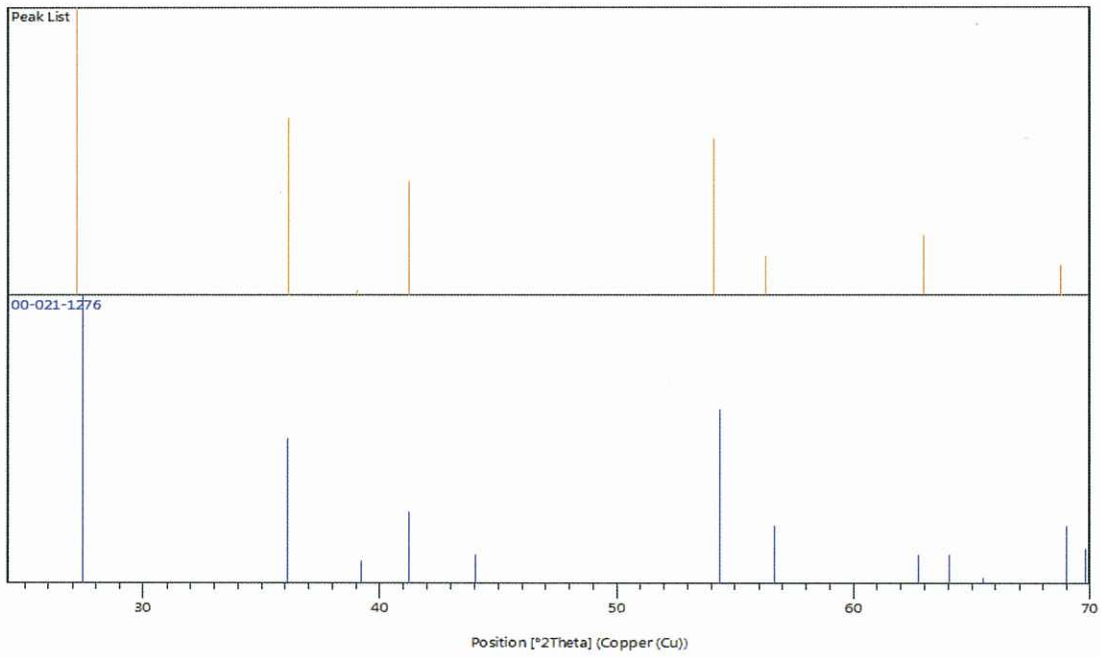
62	2	4	2	1.12735	86.202	2.5
63	2	7	1	1.12392	86.529	1.5
64	4	2	0	1.12392	86.529	1.5
65	0	6	2	1.11739	87.161	0.8
66	2	8	0	1.09526	89.385	0.8
67	4	3	0	1.08992	89.942	0.3

Stick Pattern



Appendix B Phase matched data

M122439_001



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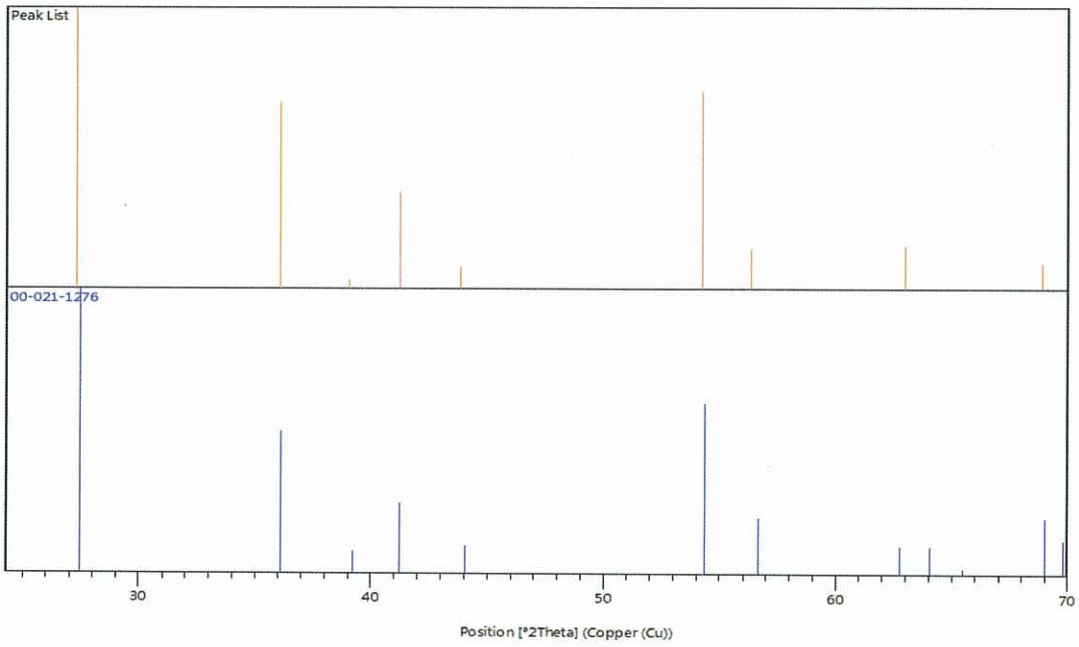

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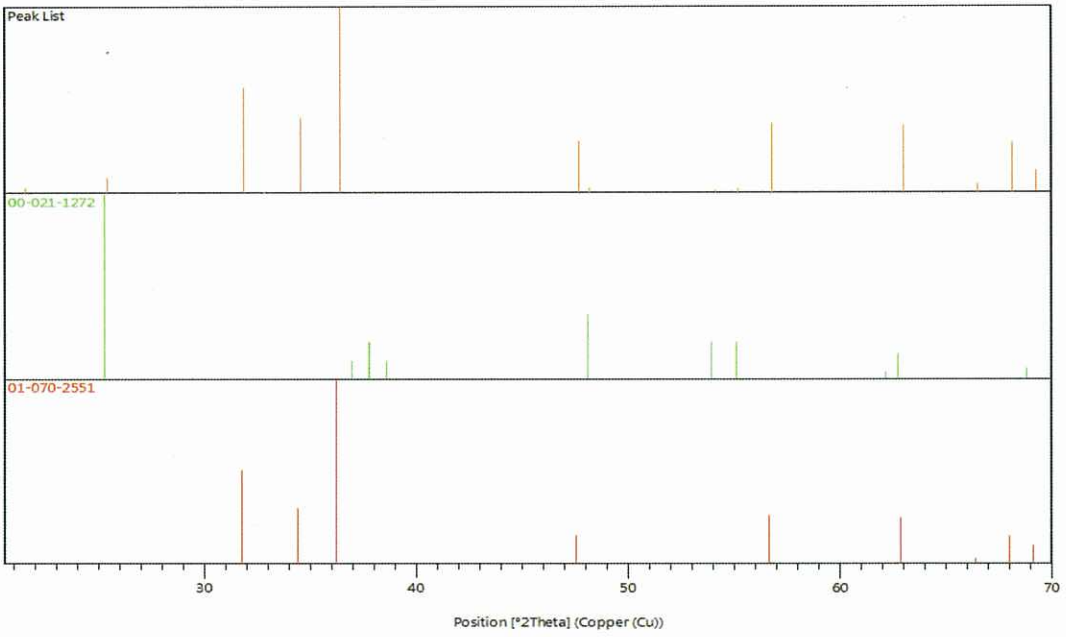

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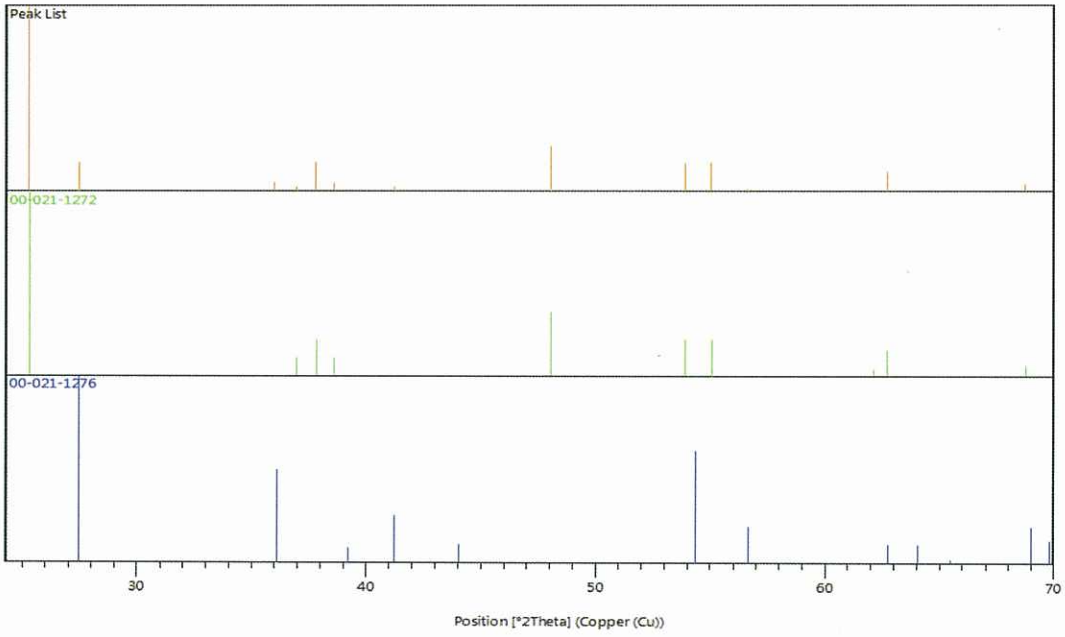

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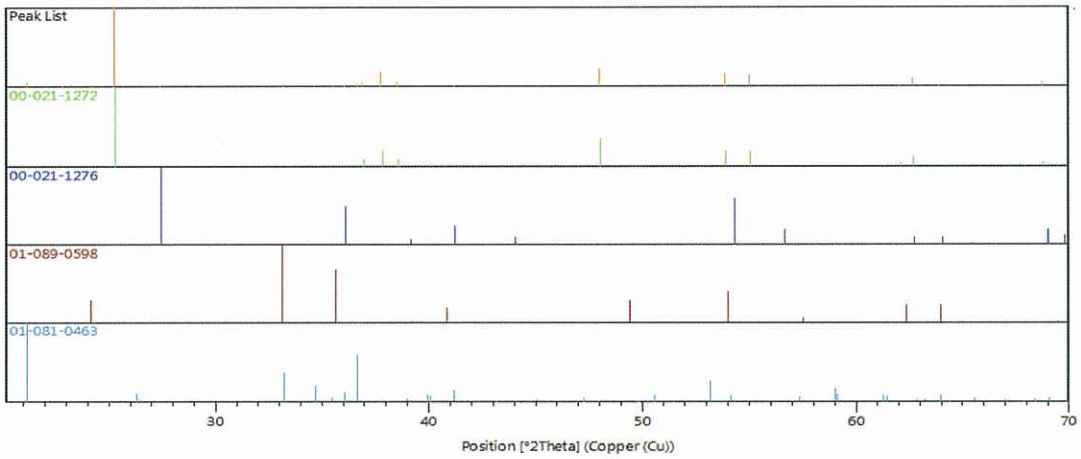

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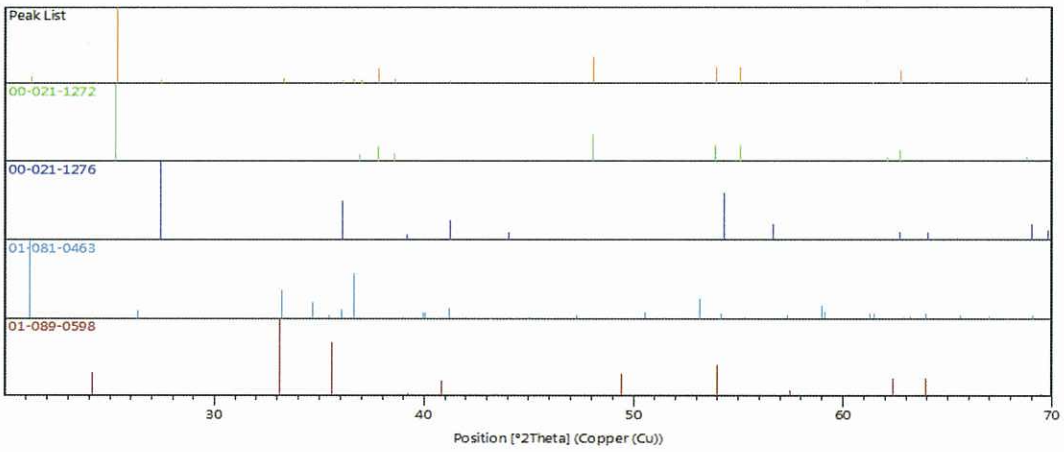
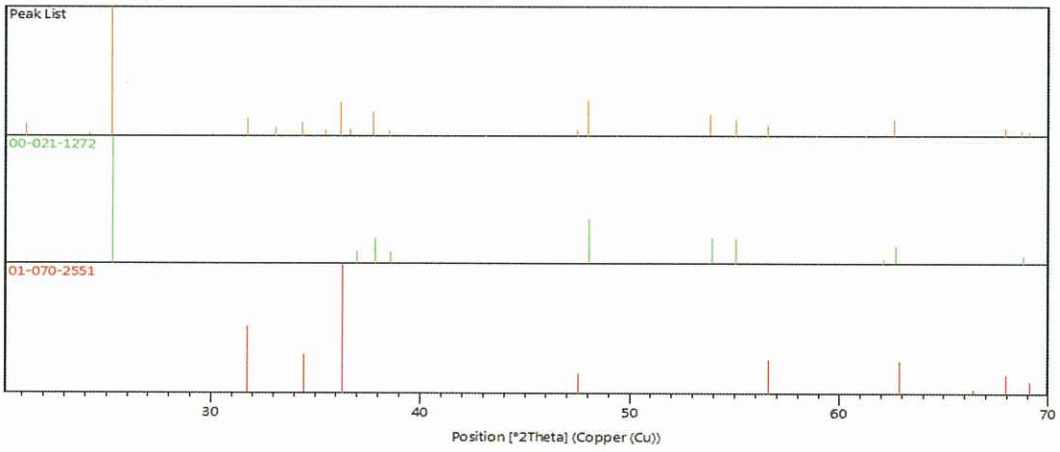
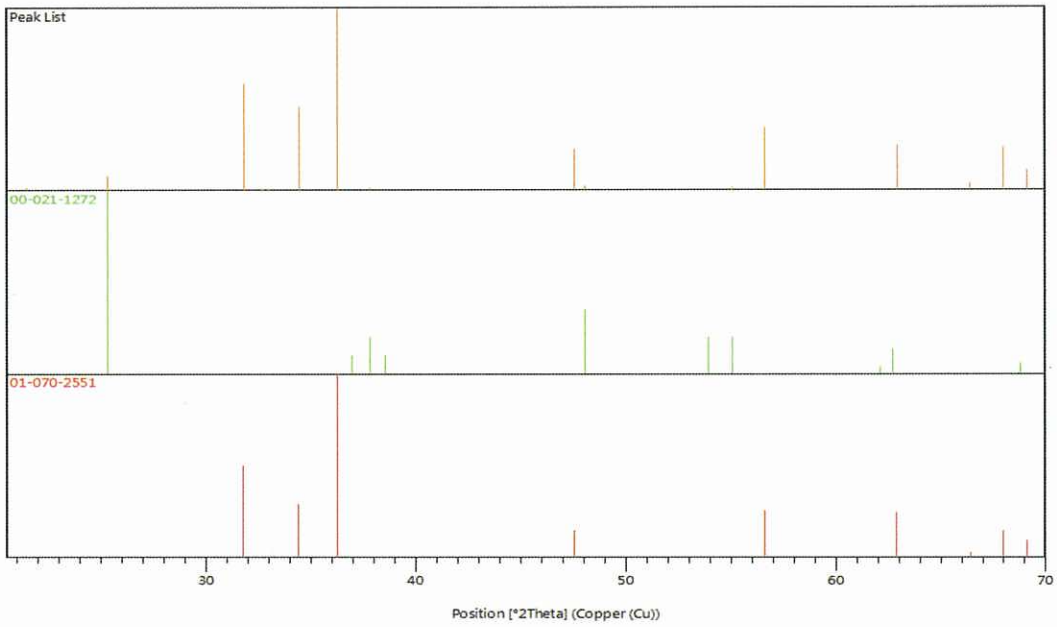


M122439_008



M122439_010


Peak List
00-021-1272
01-070-2551
30
40
50
60
70
Position [°2Theta] (Copper (Cu))