UCRL-CR-139069-SUP

Supplment to Interim Report on Task 1.3: Equilibrium Phase Diagram to Lawrence Livermore National Laboratory for Contract B345772

M. W. A. Stewart, E. R. Vance, and R. A. Day

April 18, 1999

U.S. Department of Energy

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This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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materials division

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to Lawrence Livermore National Laboratory for
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M W A Stewart, E R Vance and R A Day

18 April 1999

R99m023

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002257

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DATE ISSUED
18 April 1999

ISSUED TO
Lawrence Livermore National Laboratory

REPORT NUMBER
R99m023

JOB NUMBER
713m

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Task 1: Immobilised Form Development

Supplementary Report

Task 1.3 Equilibrium Phase Diagram

1 Summary

This report contains a summary of the results generated so far on the $CaHfTi_2O_7$ – $Gd_2Ti_2O_7$ System.

2 Experimental

Samples were made using alkoxides and nitrates (Table 1), via the alkoxide-route discussed in a previous report[1]. Compositions made are given in Table 2.

Analysis was carried out by x-ray diffraction (XRD) and scanning electron microscopy SEM), with energy dispersive x-ray spectrometry (EDS) used for quantitative analysis. Details have been given previously [1].

Samples were sintered on Pt foil in air at 1500°C for 100 hours.

Table 1: Raw materials used in Task 1.3

Element	Raw Materials for Alkoxide-route Batches (raw material, source, catalogue number)
Ca	99 % $Ca(NO_3)_2.4H_2O$, Aldrich Chem. Co., 23712-4
Gd	99.9 % $Gd(NO_3)_3.6H_2O$, Aldrich Chem., 21159-1
Hf	99.99 % Hafnium n-butoxide, Gelest Inc.
Ti	Titanium isopropoxide, HÜLS Troisdorf Gmb., 405514

3 Results and Discussion

The phases detected in the samples are given in Table 2. The EDS results are given in Tables 3 to 5. Typical microstructures are given in Figures 1 to 4. The x-ray diffraction paterns for the sample are given in Appendix A.

There are well defined transition zones with 4M zirconolite appearing in the $Ca_{0.45}Gd_{1.1}Hf_{0.45}Ti_2O_7$ sample and 2M zirconolite appearing in the $Ca_{0.8}Gd_{0.4}Hf_{0.8}Ti_2O_7$ sample. For the zirconolite composition ($Ca_zGd_yHf_xTi_2O_7$), the 4M polytype covers the approximate range $0.5 < x < 0.66$. The 2M polytype occurs for $x > 0.8$.

[1] M.W.A. Stewart, E.R. Vance, R.A. Day and A. Brownscombe, "Interim Report on Task 1.2: Near equilibrium Requirements, ANSTO Report No. R99m012, 5 April, 1999.

The pyrochlore composition is close to the design composition. The maximum amount of Hf measured in the pyrochlore in the samples was 0.42 formula units.

Excess rutile samples mws980400 and 401 show some zoning around the edges of the grains (tables 3 and 4). This was not observed in samples without excess rutile.

The rutile incorporates some hafnium (Table 5) and hence, in samples made with excess titania, the pyrochlore and zirconolite are deficient in hafnia, relative to the designed composition (Tables 3 and 4). The rutile composition is relatively constant (~ $Hf_{0.1}Ti_{0.9}O_2$) except near the zirconolite end of the test spectrum, where the rutile has slightly more Hf (Table 5). The rutile in samples made with excess titania has slightly less Hf.

4 Conclusion

The pyrochlore-zirconolite boundary is observed at approximately -

$0.6(Gd_{0.6}Ti_2O_7) + 0.4(CaHfTi_2O_7)$.

Table 2: Compositions tested and phases detected in SEM

Sample No.	Pyrochlore	Excess TiO_2 or HfO_2 (wt. %)	Phases detected
mws980399	$Ca_{0.3}Gd_{1.4}Hf_{0.3}Ti_2O_7$	18.2 % TiO_2	Pyrochlore + rutile
mws980420	$Ca_{0.3}Gd_{1.4}Hf_{0.3}Ti_2O_7$	2 % HfO_2	Pyrochlore + rutile
mws980403	$Ca_{0.35}Gd_{0.3}Hf_{0.35}Ti_2O_7$		Pyrochlore + rutile
mws980400	$Ca_{0.4}Gd_{1.2}Hf_{0.4}Ti_2O_7$	18.6 % TiO_2	Pyrochlore + rutile
mws980421	$Ca_{0.4}Gd_{1.2}Hf_{0.4}Ti_2O_7$	2 % HfO_2	Pyrochlore + rutile
mws980402	$Ca_{0.45}Gd_{1.1}Hf_{0.45}Ti_2O_7$		Pyrochlore + 4M zirconolite + rutile
mws980401	$Ca_{0.5}Gd_{1.0}Hf_{0.5}Ti_2O_7$	18.9 % TiO_2	Pyrochlore + 4M zirconolite + rutile
mws980422	$Ca_{0.5}Gd_{1.0}Hf_{0.5}Ti_2O_7$	2 % HfO_2	Pyrochlore + 4M zirconolite + rutile
mws980423	$Ca_{0.6}Gd_{0.8}Hf_{0.6}Ti_2O_7$		4M zirconolite + rutile
mws980424	$Ca_{0.7}Gd_{0.6}Hf_{0.7}Ti_2O_7$		4M zirconolite + rutile
mws980425	$Ca_{0.8}Gd_{0.4}Hf_{0.8}Ti_2O_7$		2M zirconolite + 4M zirconolite + rutile

Table 3: Composition of pyrochlore phase in the samples

Sample No.	Pyrochlore	Excess TiO_2 or HfO_2 (wt. %)	Pyrochlore composition
mws980399	$Ca_{0.3}Gd_{1.4}Hf_{0.3}Ti_2O_7$	18.2 % TiO_2	$Ca_{0.29}Gd_{1.42}Hf_{0.22}Ti_{2.07}O_7$
mws980420	$Ca_{0.3}Gd_{1.4}Hf_{0.3}Ti_2O_7$	2 % HfO_2	$Ca_{0.28}Gd_{1.43}Hf_{0.32}Ti_{1.96}O_7$
mws980403	$Ca_{0.35}Gd_{1.3}Hf_{0.35}Ti_2O_7$		$Ca_{0.35}Gd_{1.34}Hf_{0.35}Ti_{2.00}O_7$
mws980400	$Ca_{0.4}Gd_{1.2}Hf_{0.4}Ti_2O_7$	18.6 % TiO_2	$Ca_{0.40}Gd_{1.29}Hf_{0.29}Ti_{2.04}O_7$ darker zone around edge of pyrochlore grains - $Ca_{0.44}Gd_{1.20}Hf_{0.27}Ti_{2.11}O_7$
mws980421	$Ca_{0.4}Gd_{1.2}Hf_{0.4}Ti_2O_7$	2 % HfO_2	$Ca_{0.40}Gd_{1.26}Hf_{0.41}Ti_{1.95}O_7$
mws980402	$Ca_{0.45}Gd_{1.1}Hf_{0.45}Ti_2O_7$		$Ca_{0.44}Gd_{1.19}Hf_{0.40}Ti_{1.98}O_7$
mws980401	$Ca_{0.5}Gd_{1.0}Hf_{0.5}Ti_2O_7$	18.9 % TiO_2	$Ca_{0.46}Gd_{1.14}Hf_{0.35}Ti_{2.06}O_7$
mws980422	$Ca_{0.5}Gd_{1.0}Hf_{0.5}Ti_2O_7$	2 % HfO_2	$Ca_{0.42}Gd_{1.19}Hf_{0.42}Ti_{1.97}O_7$
mws980423	$Ca_{0.6}Gd_{0.8}Hf_{0.6}Ti_2O_7$		NIL
mws980424	$Ca_{0.7}Gd_{0.6}Hf_{0.7}Ti_2O_7$		NIL
mws980425	$Ca_{0.8}Gd_{0.4}Hf_{0.8}Ti_2O_7$		NIL

Table 4: Composition of zirconolite phases in the samples

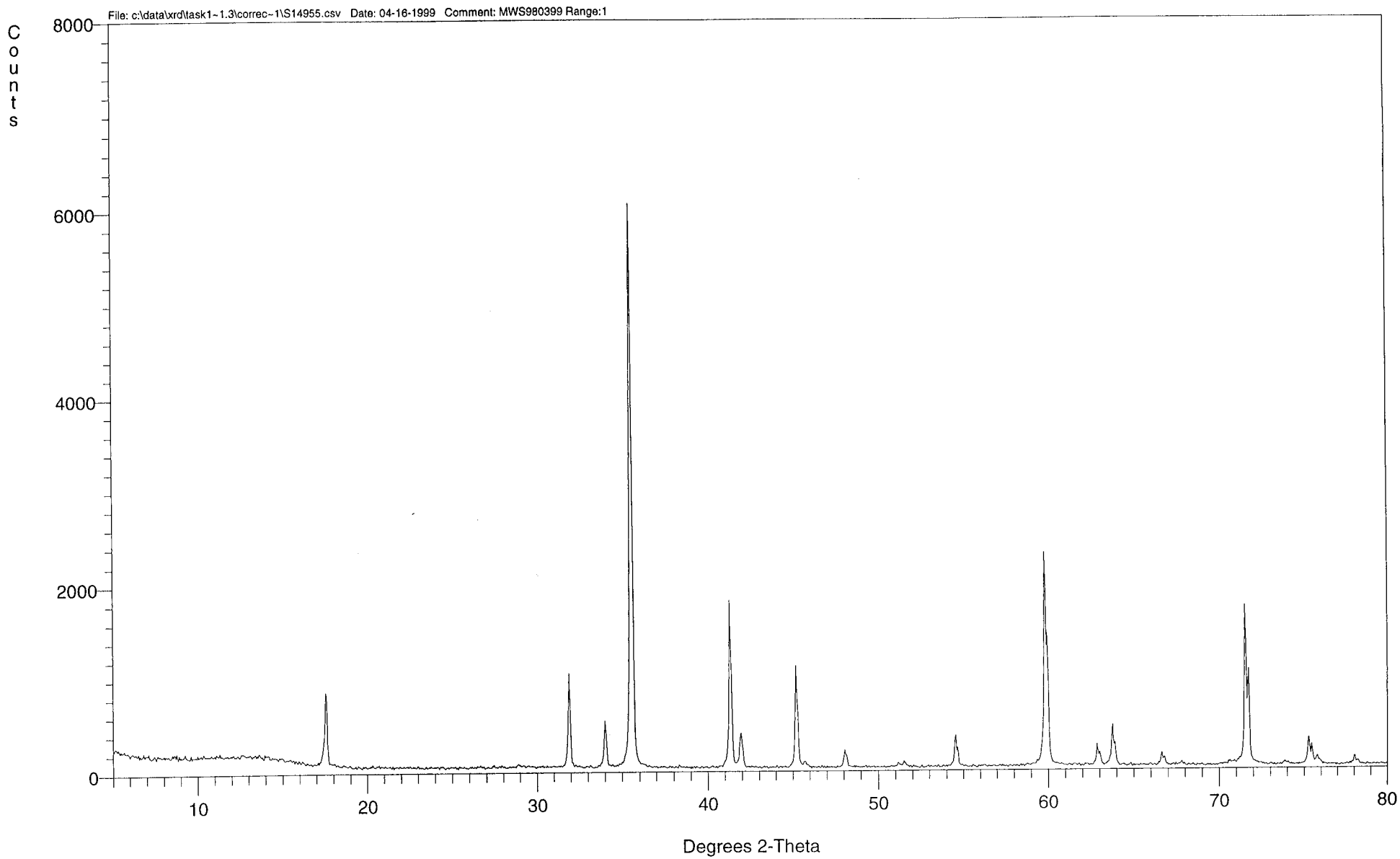
Sample No.	Pyrochlore	Excess TiO_2 or HfO_2 (wt. %)	Zirconolite composition Polytype
mws980399	$Ca_{0.3}Gd_{1.4}Hf_{0.3}Ti_2O_7$	18.2 % TiO_2	NIL
mws980420	$Ca_{0.3}Gd_{1.4}Hf_{0.3}Ti_2O_7$	2 % HfO_2	NIL
mws980403	$Ca_{0.35}Gd_{1.3}Hf_{0.35}Ti_2O_7$		NIL
mws980400	$Ca_{0.4}Gd_{1.2}Hf_{0.4}Ti_2O_7$	18.6 % TiO_2	NIL
mws980421	$Ca_{0.4}Gd_{1.2}Hf_{0.4}Ti_2O_7$	2 % HfO_2	NIL
mws980402	$Ca_{0.45}Gd_{1.1}Hf_{0.45}Ti_2O_7$		4M - $Ca_{0.54}Gd_{0.86}Hf_{0.57}Ti_{1.98}O_7$
mws980401	$Ca_{0.5}Gd_{1.0}Hf_{0.5}Ti_2O_7$	18.9 % TiO_2	4M - $Ca_{0.58}Gd_{0.79}Hf_{0.49}Ti_{2.13}O_7$ Darker overgrowth 4M - $Ca_{0.58}Gd_{0.87}Hf_{0.34}Ti_{2.13}O_7$
mws980422	$Ca_{0.5}Gd_{1.0}Hf_{0.5}Ti_2O_7$	2 % HfO_2	4M - $Ca_{0.53}Gd_{0.86}Hf_{0.59}Ti_{2.00}O_7$
mws980423	$Ca_{0.6}Gd_{0.8}Hf_{0.6}Ti_2O_7$		4M - $Ca_{0.57}Gd_{0.80}Hf_{0.56}Ti_{2.05}O_7$
mws980424	$Ca_{0.7}Gd_{0.6}Hf_{0.7}Ti_2O_7$		4M - $Ca_{0.68}Gd_{0.63}Hf_{0.66}Ti_{2.02}O_7$
mws980425	$Ca_{0.8}Gd_{0.4}Hf_{0.8}Ti_2O_7$		4M - $Ca_{0.72}Gd_{0.56}Hf_{0.66}Ti_{2.05}O_7$ 2M - $Ca_{0.80}Gd_{0.29}Hf_{0.83}Ti_{2.05}O_7$

Table 5: Composition of rutile in the samples

Sample No.	Pyrochlore	Excess TiO_2 or HfO_2 (wt. %)	Rutile composition
mws980399	$Ca_{0.3}Gd_{1.4}Hf_{0.3}Ti_2O_7$	18.2 % TiO_2	$Hf_{0.06}Ti_{0.94}O_2$
mws980420	$Ca_{0.3}Gd_{1.4}Hf_{0.3}Ti_2O_7$	2 % HfO_2	$Hf_{0.10}Ti_{0.90}O_2$
mws980403	$Ca_{0.35}Gd_{1.3}Hf_{0.35}Ti_2O_7$		$Hf_{0.09}Ti_{0.91}O_2$
mws980400	$Ca_{0.4}Gd_{1.2}Hf_{0.4}Ti_2O_7$	18.6 % TiO_2	$Hf_{0.07}Ti_{0.93}O_2$
mws980421	$Ca_{0.4}Gd_{1.2}Hf_{0.4}Ti_2O_7$	2 % HfO_2	$Hf_{0.12}Ti_{0.88}O_2$
mws980402	$Ca_{0.45}Gd_{1.1}Hf_{0.45}Ti_2O_7$		$Hf_{0.11}Ti_{0.89}O_2$
mws980401	$Ca_{0.5}Gd_{1.0}Hf_{0.5}Ti_2O_7$	18.9 % TiO_2	$Hf_{0.08}Ti_{0.92}O_2$
mws980422	$Ca_{0.5}Gd_{1.0}Hf_{0.5}Ti_2O_7$	2 % HfO_2	$Hf_{0.11}Ti_{0.89}O_2$
mws980423	$Ca_{0.6}Gd_{0.8}Hf_{0.6}Ti_2O_7$		$Hf_{0.11}Ti_{0.89}O_2$
mws980424	$Ca_{0.7}Gd_{0.6}Hf_{0.7}Ti_2O_7$		$Hf_{0.13}Ti_{0.89}O_2$
mws980425	$Ca_{0.8}Gd_{0.4}Hf_{0.8}Ti_2O_7$		$Hf_{0.14}Ti_{0.86}O_2$

Appendix A – X-ray Diffraction Results

Samples were measured using a Siemens D500 Diffractometer, employing Co K-alpha radiation.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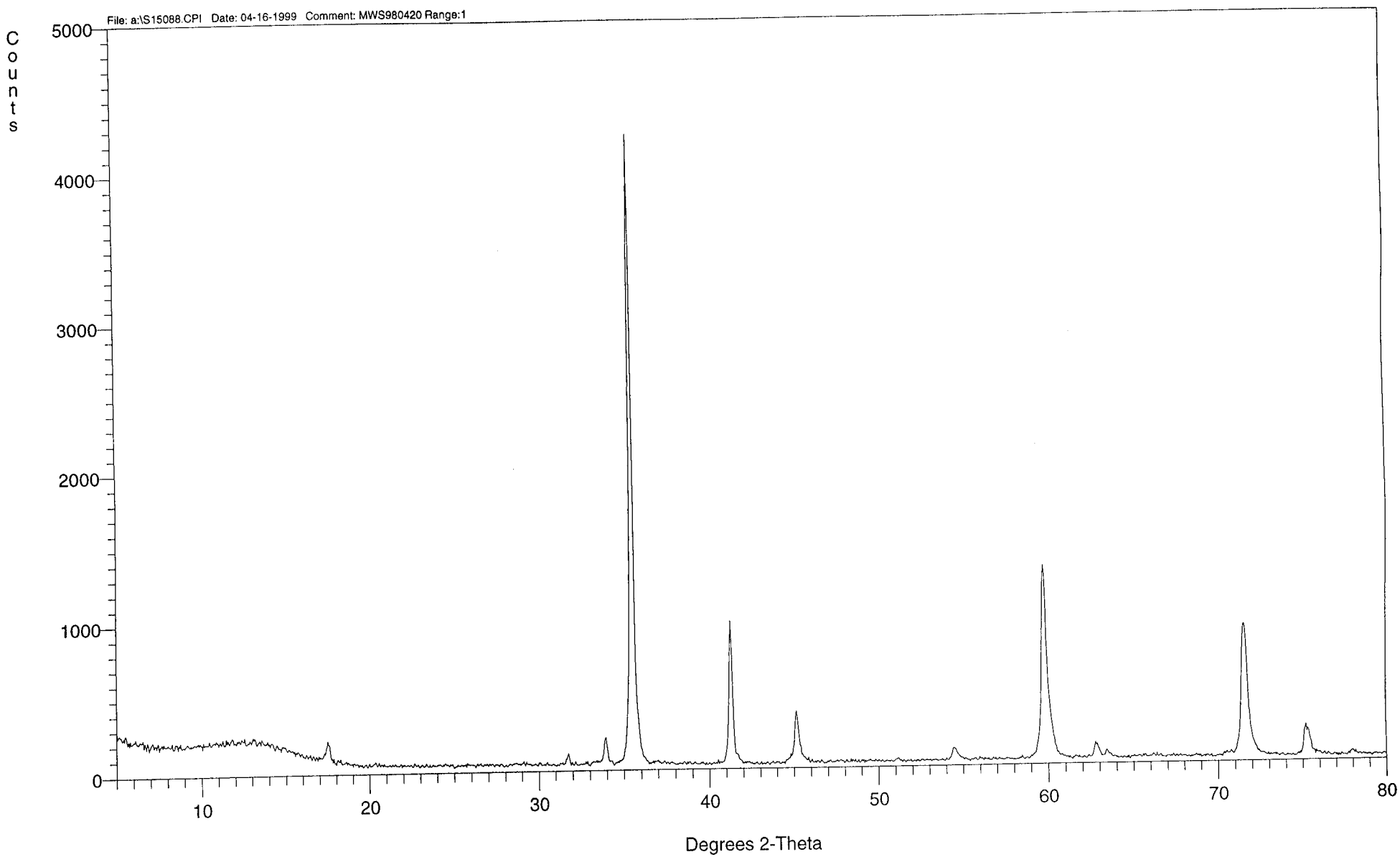
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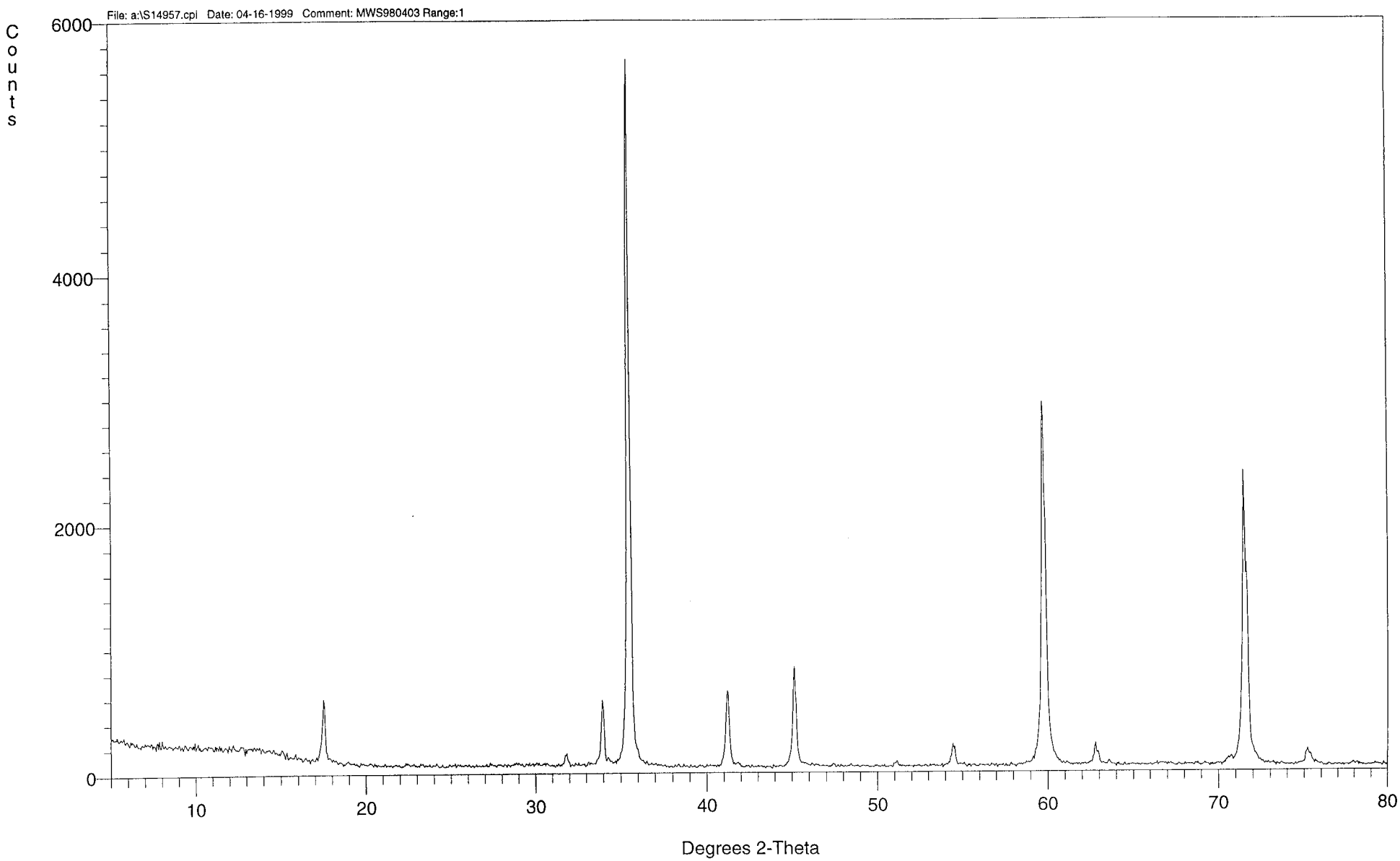
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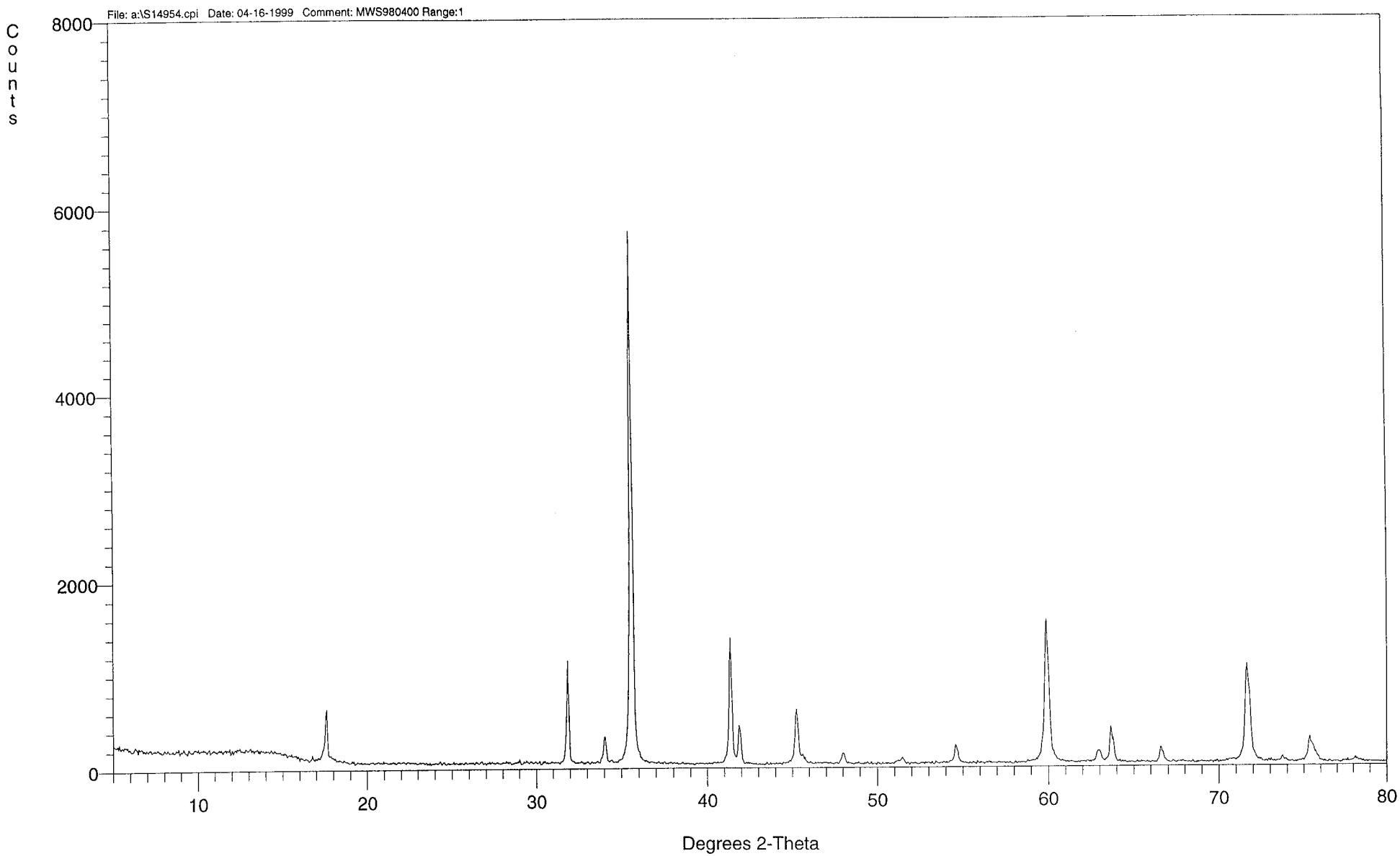
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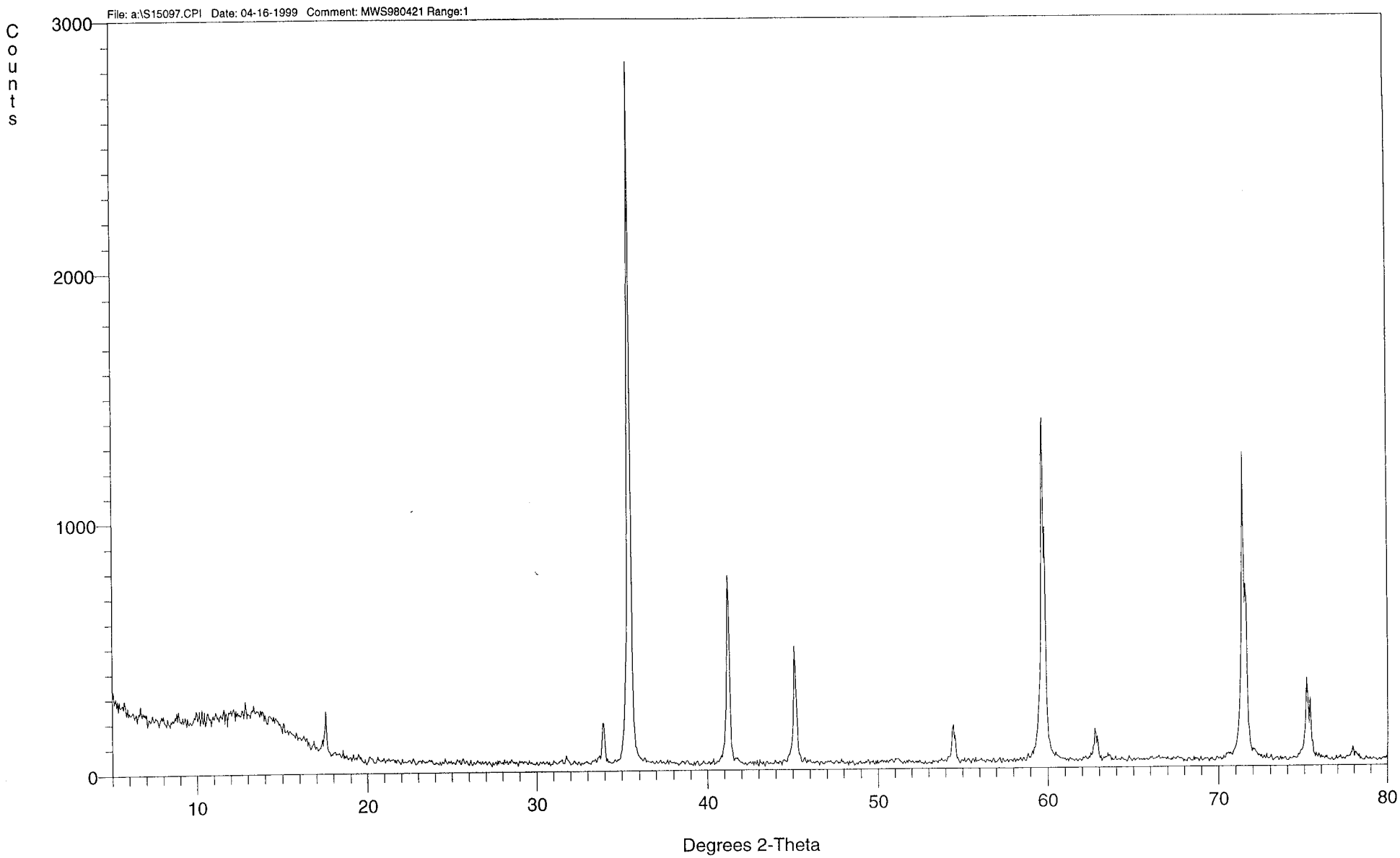
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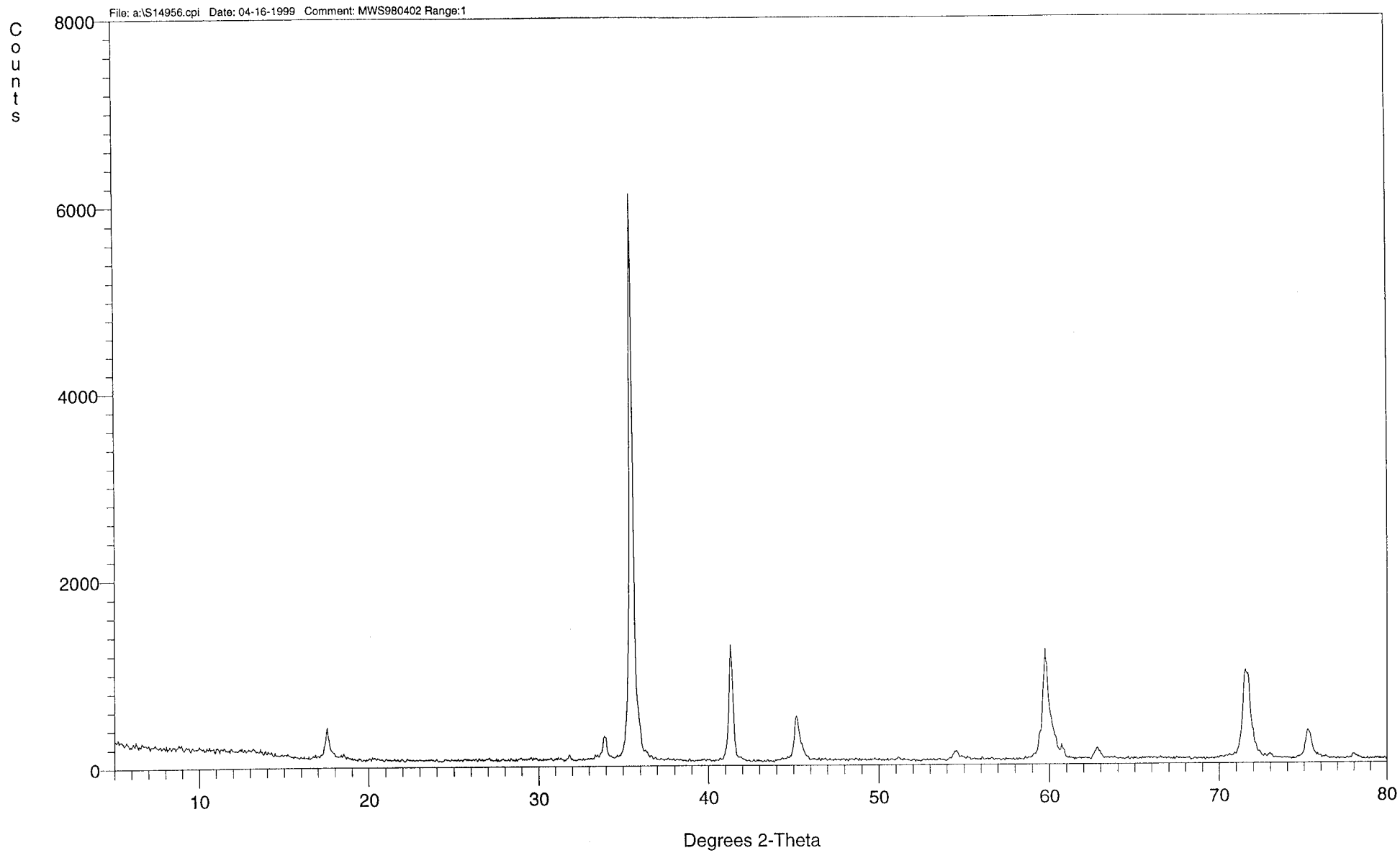
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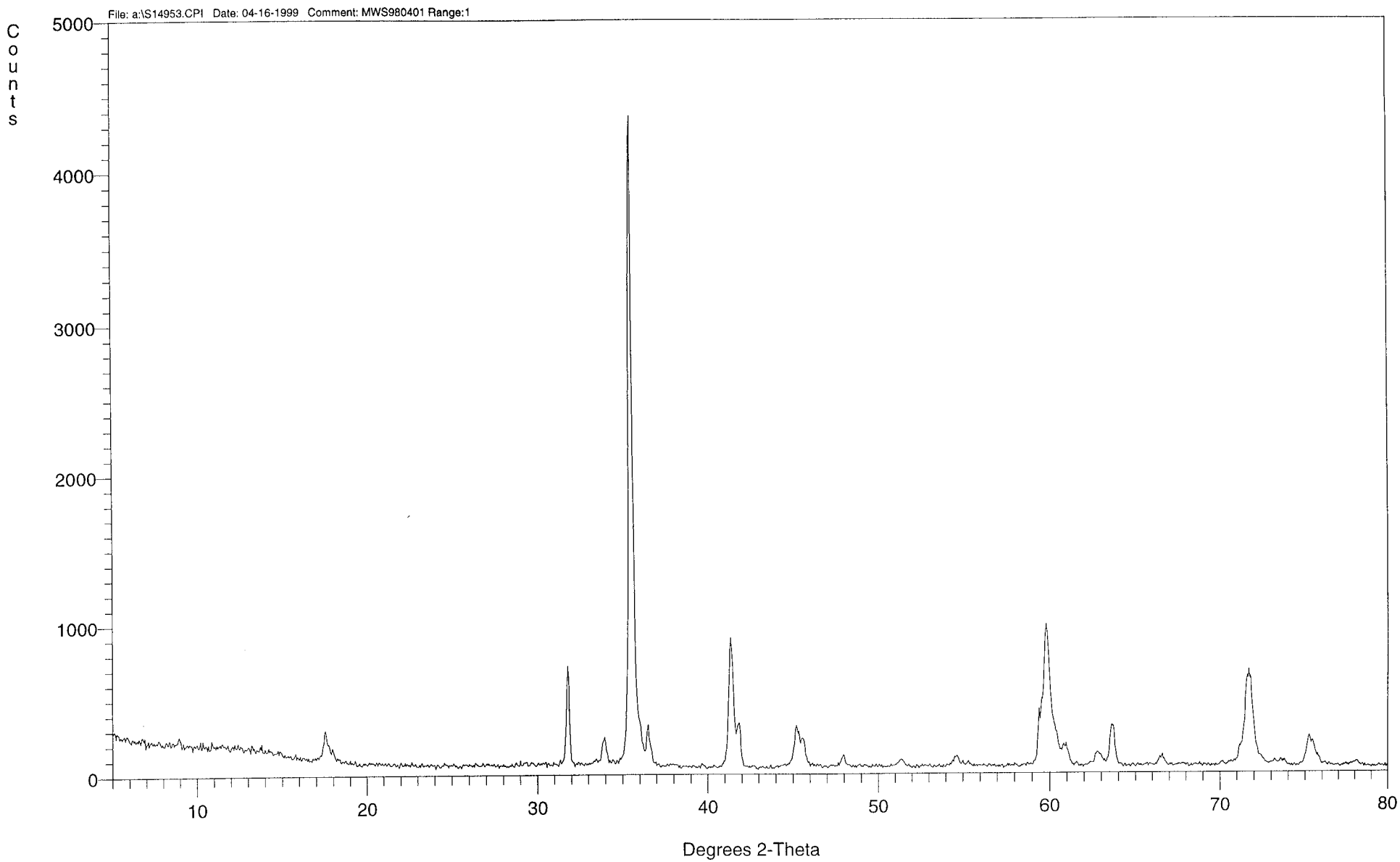
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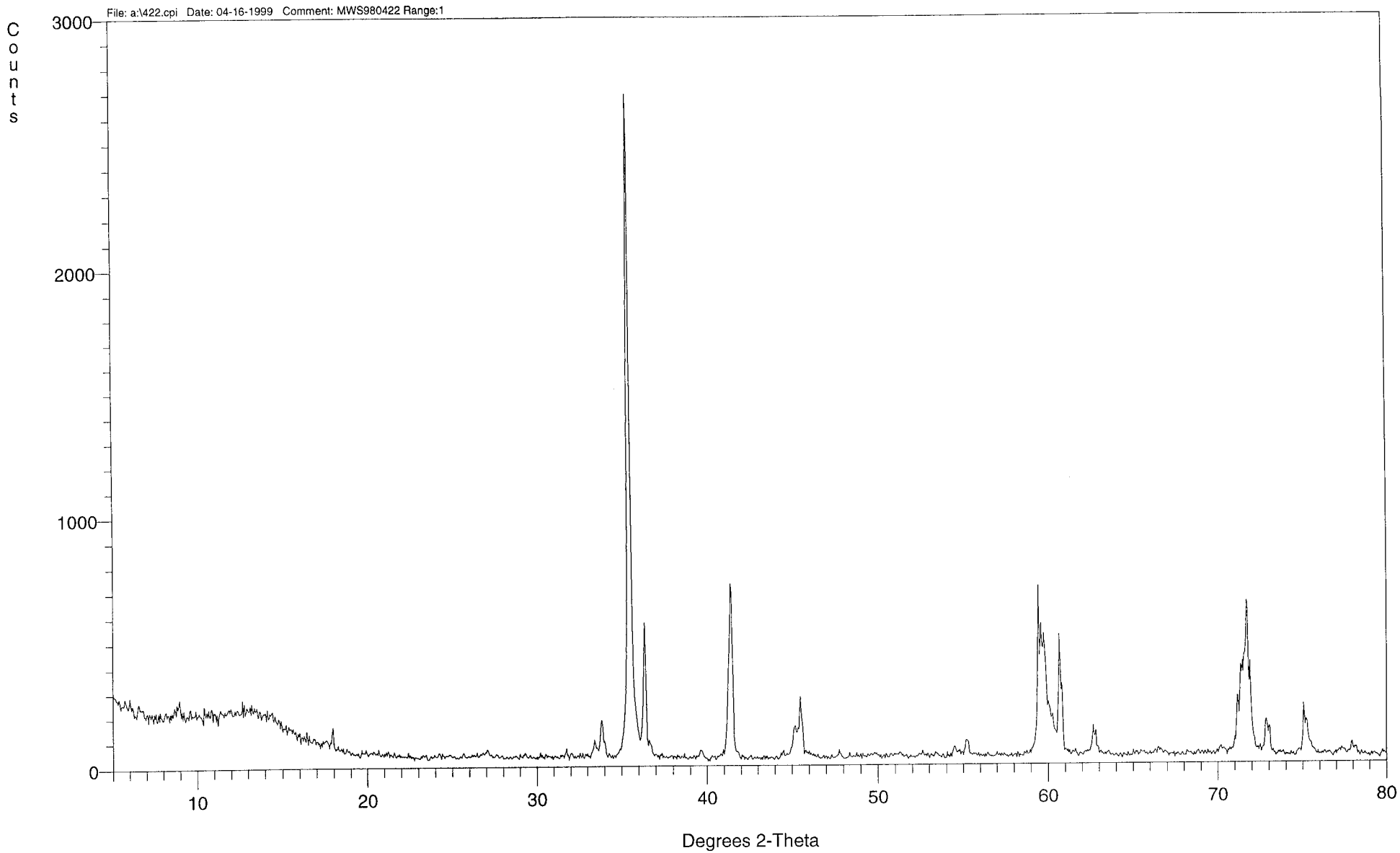
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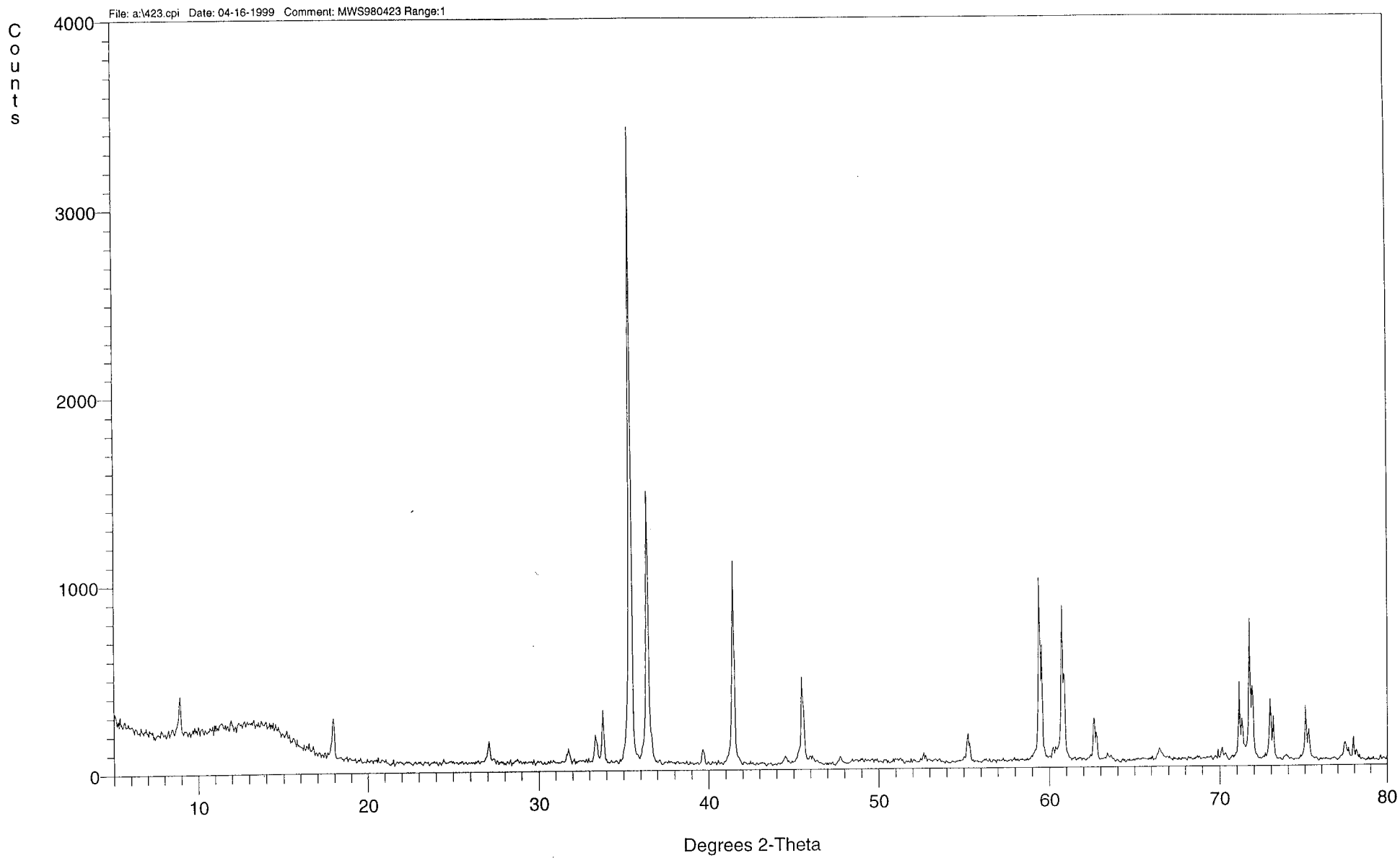
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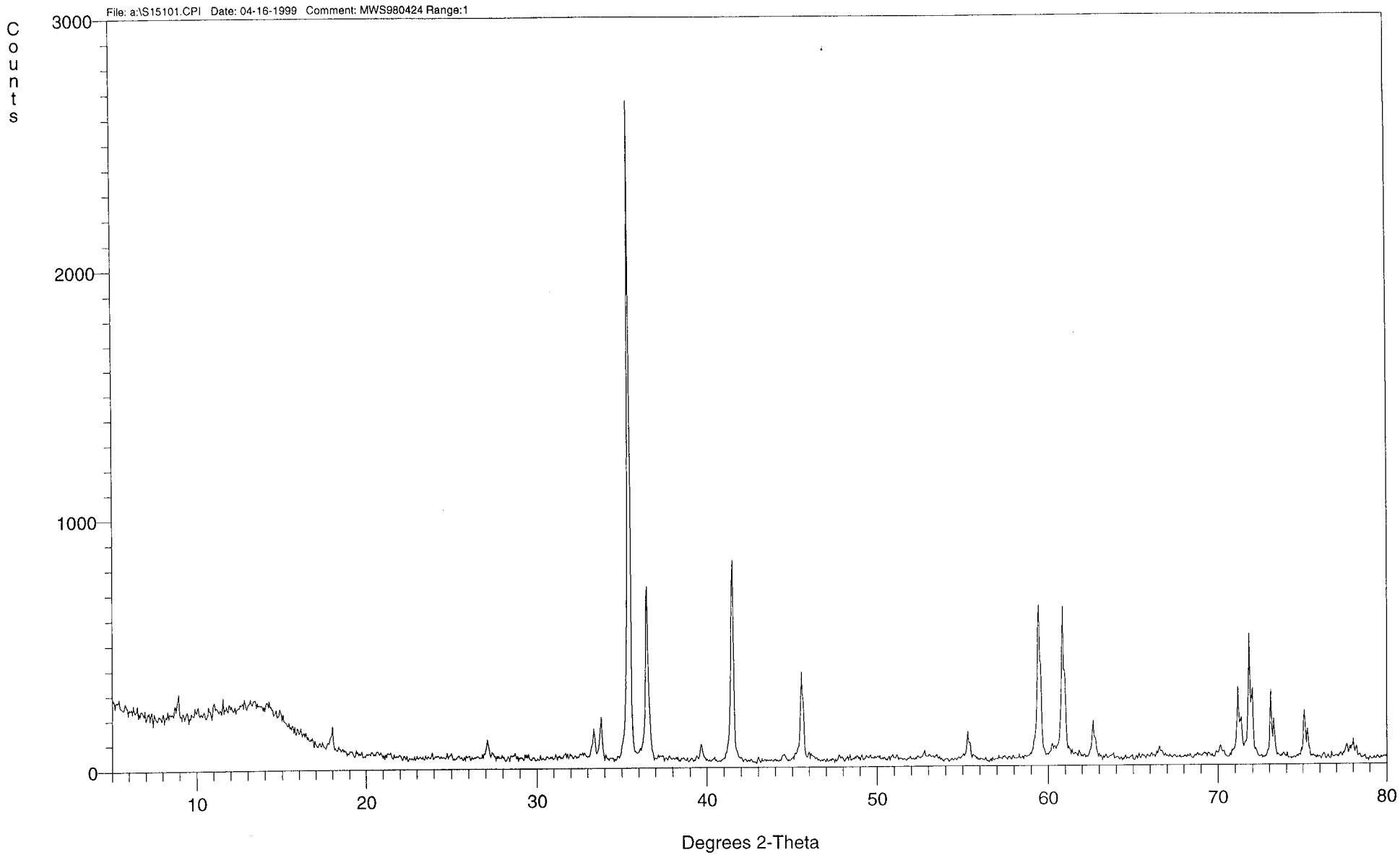
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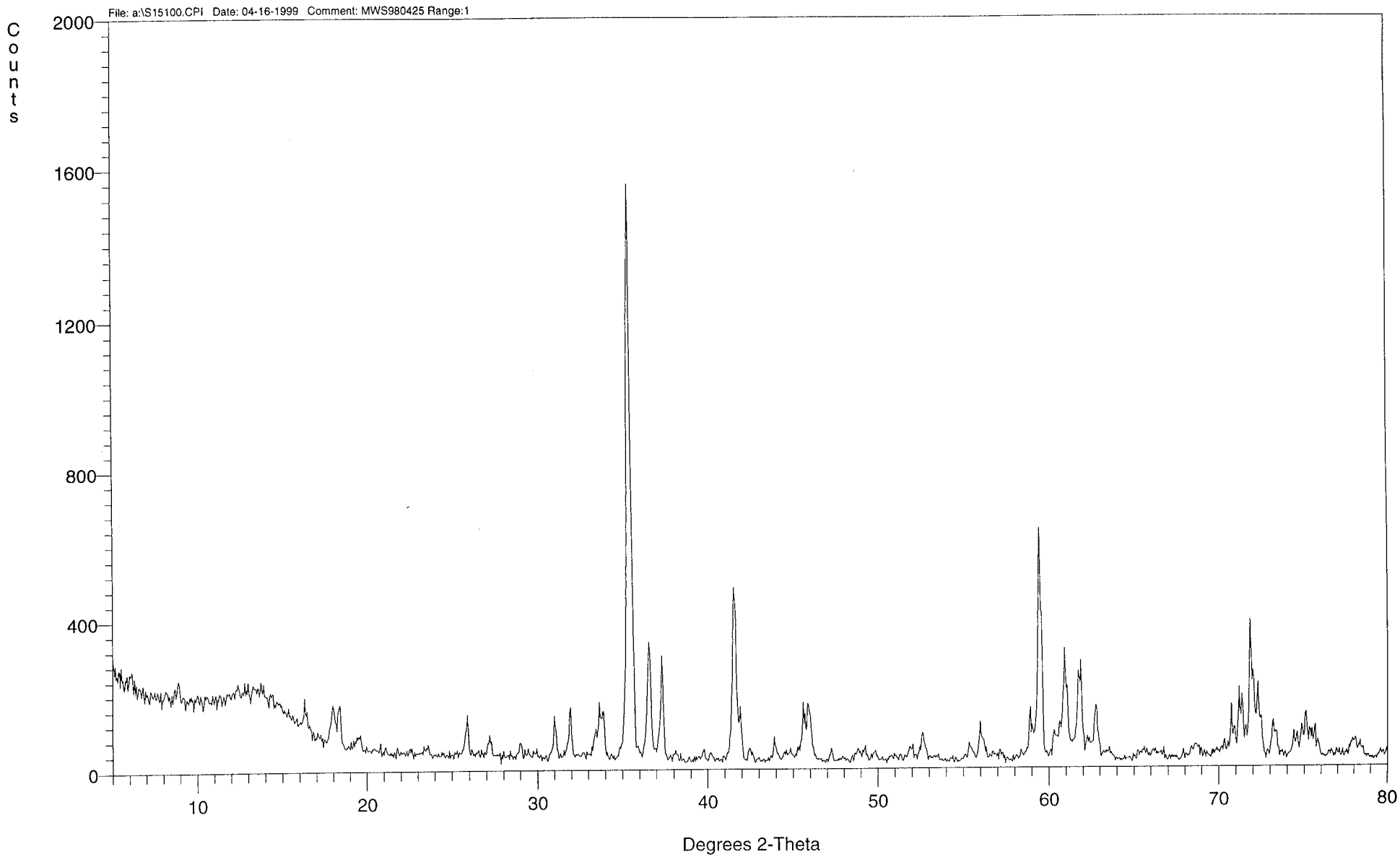
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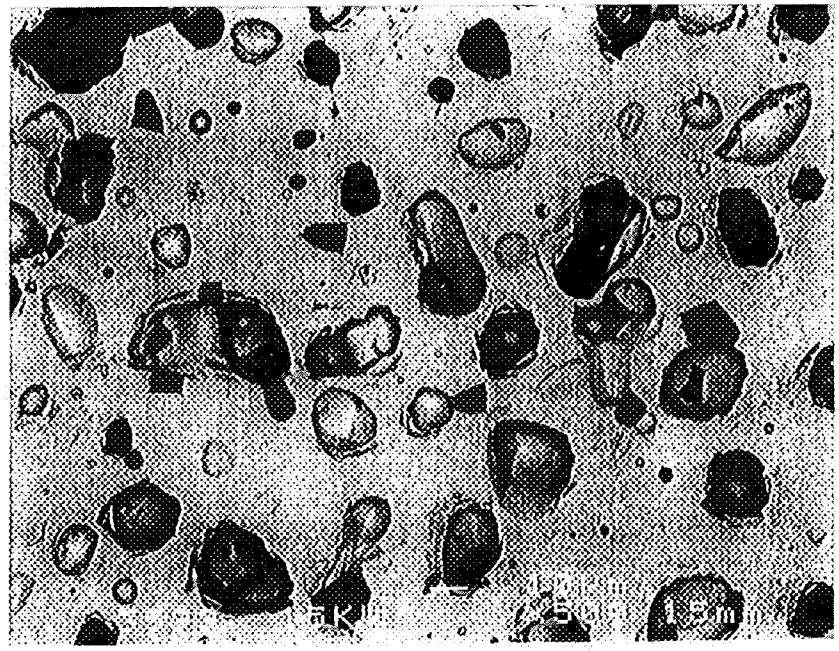

Figure 1: (a) Backscattered electron micrograph mws980420 ($Ca_{0.3}Gd_{1.4}Hf_{0.3}Ti_2O_7$ + 2 % HfO_2). The pellet consists of pyrochlore (matrix), with some rutile (dark-grey) and porosity.

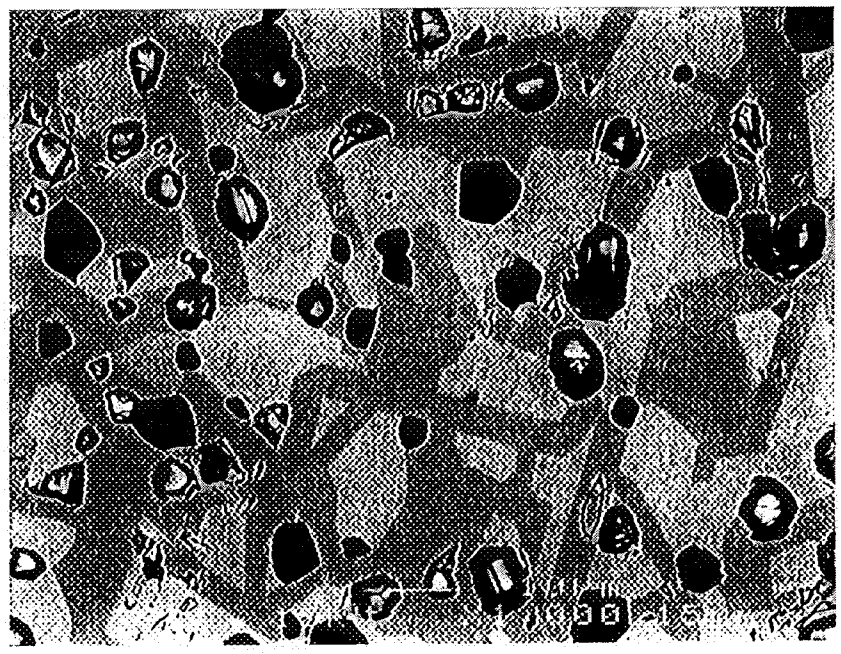

Figure 2: (a) Backscattered electron micrograph mws980422 ($Ca_{0.5}Gd_{1.0}Hf_{0.5}Ti_2O_7$ + 2 % HfO_2). The pellet consists of pyrochlore (light grey), 4M zirconolite (dark-grey) and porosity.

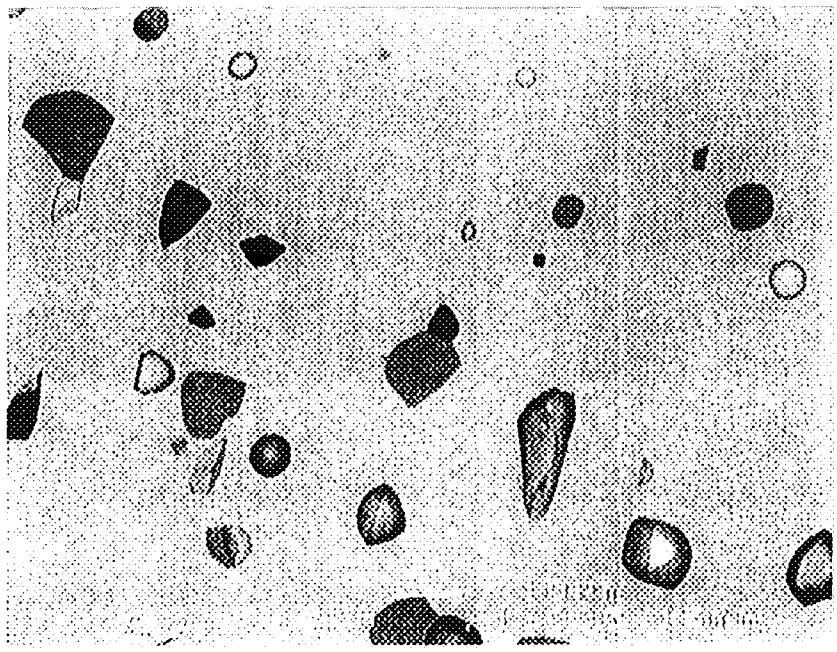

Figure 3: (a) Backscattered electron micrograph mws980423 ($Ca_{0.6}Gd_{0.8}Hf_{0.6}Ti_2O_7$). The pellet consists of a 4M zirconolite (matrix), with some rutile (dark-grey) and porosity.

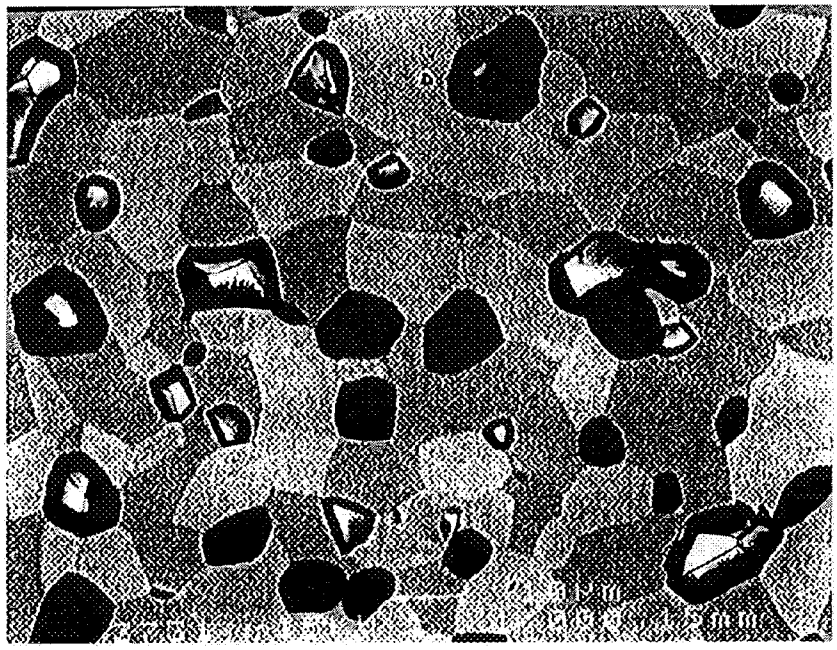

Figure 4: (a) Backscattered electron micrograph mws980425 ($Ca_{0.8}Gd_{0.4}Hf_{0.8}Ti_2O_7$). The pellet consists of 4M zirconolite (light grey), 2M zirconolite (dark-grey), rutile (dark-grey-black) and porosity.