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Report on Phase 23 of Task 1.1: Single Phase Synthesis to Lawrence Livermore National Laboratory for Contract B345772

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Report on Phase 2 of Task 1.1: Single Phase Synthesis

to Lawrence Livermore National Laboratory for Contract B345772 –

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

23 November 1999

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Australian Nuclear Science and Technology Organisation
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Task 1: Immobilised Form Development

Report on Phase 2 of Task 1.1: Single Phase Synthesis

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1 Summary

Near single phase pyrochlores and zirconolites (with Hf substituted for Zr) of the following compositions have been prepared. The results obtained are summarised in Table 1. Details of the fabrication method and the results are given below.

- Mg-doped zirconolite ($Ca_{0.4}Gd_{0.6}HfMg_{0.3}Ti_{1.7}O_7$),
- Al-doped zirconolite ($Ca_{0.5}Gd_{0.5}HfAl_{0.5}Ti_{1.5}O_7$),
- Ta-doped pyrochlore ($CaGdTaTiO_7$),
- Pu-pyrochlore ($CaPuTi_2O_7$), and
- 4M zirconolite from the Ca-Gd-Hf-Ti-O system ($Ca_{0.6}Gd_{0.8}Hf_{0.6}Ti_2O_7$ and $Ca_{0.7}Gd_{0.6}Hf_{0.7}Ti_2O_7$).

All but the Ta-doped pyrochlore were prepared via the alkoxide-route. The Ta-pyrochlore was prepared via the oxide-route.

Mo-doped pyrochlore could not be made single phase with significant amounts (0.4-0.6 formula units) of Mo present in the nominal batch pyrochlore formulation. If Ca was present powellite formed and Mg produced $MgMoO_4$. All samples basically contained a Ti-pyrochlore with a small amount (< 0.1 formula units) of Mo present, and a Mo-rich phase, which contained some Ti (Table 1).

Pu-brannerite ($PuTi_2O_6$) proved to be difficult to make. The Pu-brannerite did not form until the sintering temperature was close to the melting point, ~ 1500°C. Regions rich in Pu-brannerite could be found in some samples, though these samples invariably contained regions rich in PuO_2 and rutile. In a sample with 20 wt. % excess TiO_2, large Pu-brannerite grains were seen, presumably having grown from a melt.

Work on Sn-doped pyrochlore and zirconolite end members is continuing as part of Task 1.4 and the results have been included here for interest. The sample of nominal composition $CaSnTi_2O_7$ did not form pyrochlore or zirconolite. Instead perovskite, $SnTiO_4$ and Ti-doped SnO_2 were formed. The sample of nominal composition $CaHfSn_2O_7$ was very refractory, with little densification occurring upon sintering, even after sintering at 1600°C. The samples remained porous and very soft and friable. The sample sintered at 1600°C appeared to be near single phase, but there was some compositional variation across the sample was observed. This sample was re-milled and the refired at 1600°C for 16 hours in air. This sample was much denser. The XRD pattern indicated that it was composed mainly of zirconolite plus some minor (Hf,Sn)TiO_4.

Samples of the Mg-doped zirconolite, Al-doped zirconolite, Ta-doped pyrochlore and two 4M zirconolite samples from the Ca-Gd-Hf-Ti-O system have been shipped to LLNL.

Table 1: Summary of the results obtained for the pyrochlore and zirconolite compositions made.

Nominal Composition of the major phase $^{\$}$	Prep. Route	Sint. Temp. (°C)/ time (h.) *	Results
Al-doped Zirconolite			
$Ca_{0.5}Gd_{0.5}HfAl_{0.5}Ti_{1.5}O_7$	oxide	1350/50	2M zirconolite + Hf-doped rutile + $HfTiO_4$.
“	“	1400/16	X-ray pattern is similar to that of the 1350°C/50 h sample but also has perovskite peaks.
$^{\#}Ca_{0.5}Gd_{0.5}HfAl_{0.5}Ti_{1.5}O_7$	alkoxide	1350/50	2M Zirconolite + ~ 1-2 vol. % $HfTiO_4$.
Mg-doped Zirconolite			
$^{\#}Ca_{0.4}Gd_{0.6}HfMg_{0.3}Ti_{1.7}O_7$	alkoxide	1350/50	2M Zirconolite and << 1 vol. % HfO_2 which contains some Ti.
Ta-doped pyrochlore			
$CaGdTaTiO_7$	oxide	1400/48	Pyrochlore + some additional x-ray peaks.
“	“	1450/48	Pyrochlore only (on x-ray pattern).
#“	“	1500/48	Pyrochlore and .
Mo-doped pyrochlore			
Mo at 4+			
$Gd_2Ti_{1.5}Mo_{0.5}O_7$	oxide	1450/ 8 Sint. in Argon	A mixture of $Gd_2Ti_{0.9}Mo_{1.1}O_7$ and $Gd_2Ti_{1.9}Mo_{0.1}O_7$.
Mo at 6⁺			
$Gd_2Ti_{1.5}Mo_{0.5}O_{7+x}$	oxide	1450/50	Not single-phase pyrochlore - by XRD. XRD pattern is different to the sample sintered in Ar (see above).
“	alkoxide	1450/16	This was composed of $Gd_2Ti_2O_7$ pyrochlore with a trace of Mo (~ 0.02 formula units) and a phase of composition ~ $Gd_{1.7}Ti_{0.9}Mo_{0.9}O_7$. The XRD pattern is similar to the sample fired in Ar.
$CaGdTi_{1.5}Mo_{0.5}O_7$	oxide	1400 and 1450/48	XRD pattern reveals pyrochlore, powellite ($CaMoO_4$) and probably perovskite.
$Gd_2TiMg_{0.5}Mo_{0.5}O_7$	alkoxide	1450/16	Composed of $MgMoO_4$, $Mg_{0.25}Gd_{1.79}Mo_{0.31}Ti_{1.58}O_7$, and $Gd_{1.80}Mo_{0.98}Ti_{0.18}O_6$.
$Gd_2TiMg_{0.5}Mo_{0.5}O_7$	alkoxide	1450/50	X-ray is similar to the 16 hour sinter
$Gd_2Ti_{0.8}Al_{0.8}Mo_{0.4}O_7$	alkoxide	1450/16	Appears to consist of two phases, one of which is a pyrochlore with ~ 0.09 formula units of Mo and the other is an unidentified Mo-rich phase.
“	“	1450/50	XRD pattern is similar to the 16 hour sinter above

Pu-pyrochlore			
$CaPuTi_2O_7$	alkoxide	1490/16	Near single phase $CaPuTi_2O_7$ with < 1 vol. % each of PuO_2 and TiO_2.
Pu-brannerite			
$PuTi_2O_6$	alkoxide	1500,1550/16	samples consist of $PuTi_2O_6$, PuO_2 and TiO_2. Max. yield ~ 70 % brannerite.
$PuTi_2O_6$ + 20 wt. % excess TiO_2	alkoxide	1500,1525/4-16	Complex results, difficult to form as a single phase Samples consist of $PuTi_2O_6$, PuO_2 and TiO_2. In the 1525°C sample some regions free of PuO_2 can be found growing from the melt. Melted regions appear to have resulted in the decomposition of the brannerite to oxides.
$PuTi_2O_6$ + 3wt. % excess TiO_2	alkoxide	1400,1490,1525/4-16	1525°C sample melted. 1490°C sample consists of $PuTi_2O_6$, PuO_2 and TiO_2. Regions of ~ 95 % brannerite can be found in the sample. Melted regions appear to have resulted in the decomposition of the brannerite.
4M Zirconolite			
#$Ca_{0.6}Gd_{0.8}Hf_{0.6}Ti_{2.0}O_7$	alkoxide	1500/100	Samples consisted of 4M zirconolite and ~ 3 vol. % Hf-doped rutile
#$Ca_{0.7}Gd_{0.6}Hf_{0.7}Ti_{2.0}O_7$	alkoxide	1500/100	Samples consisted of 4M zirconolite and ~ 3 vol. % Hf-doped rutile
Sn-based pyrochlore and zirconolite Structures			
$CaSnTi_2O_7$	Alkoxide/oxide	1450,1525/16-50	Not single phase, mixture of perovskite, what appears to be $SnTiO_4$ and Ti-doped SnO_2
$CaHfSn_2O_7$	Alkxoide/oxide	1600/4 and 16	Appears to be near single-phase zirconolite with compositional variations across the pellet.

\# samples sent to LLNL

$ All these samples have been made with excess TiO_2, see footnote 1 below.

* Samples were sintered in air unless otherwise stated.

2 Introduction

This report contains a summary of the results generated in phase 2 of Task 1.1

We have attempted to prepare by subsolidus ceramic processing single phases[1] of:

- Mg-doped zirconolite (with Hf substituted for Zr)
- Al-doped zirconolite (with Hf substituted for Zr)
- Ta-doped pyrochlore
- Mo-doped pyrochlore (separate samples containing "nominally Mo^{4+} and Mo^{6+})
- Pu-pyrochlore ($CaPuTi_2O_7$)
- Pu-brannerite ($PuTi_2O_6$)
- 4M zirconolite from the Ca-Gd-Hf-Ti-O system
- Sn-doped pyrochlore and zirconolite end members

The results obtained have been summarised in Table 1 above. Details on the fabrication methods are given below.

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[1] 1 wt. % excess TiO2 was added to all the batches, except the Pu-pyrochlore, which contained 4 wt. % excess TiO2 and the Pu-brannerite were various amounts of excess TiO_2 were added in an attempt to react all the PuO_2.

3 Experimental Methods

Samples were prepared via alkoxide and oxide-routes. Details of these methods have been given elsewhere[2].

3.1 Alkoxide-Route Wet-milled Powder Preparation

Batches of ~ 20 g (oxide basis) were made for each of the batches.

The alkoxide precursors were made as follows. The Ti and/or Hf alkoxides were mixed together and diluted to 50 % by adding anhydrous ethanol. The required non-radioactive chemicals (Table 2) were mixed together in deionised water and added to the alkoxides. The batch was then shear mixed for 10 minutes.

If the batch was a Pu-doped batch the sample was dried on a hot plate to remove the bulk of the alcohol prior to placing it in the glove box. Note that the sample was dried to a creamy paste, not fully dry. It was taken to the Actinide Suite where Pu was added to the precursor as a Pu-nitrate solution. This slurry was then thoroughly mixed using a magnetic stirrer and then dried to remove the nitric acid and water. A condenser was used to collect the nitric acid.

The non-radioactive samples were then also dried on a hot-plate and then in an oven to 110 - 120°C.

The resulting dried powders were placed in an alumina container and calcined in air for 1 hour at 750°C. Pu-doped materials were calcined in an alumina tube furnace. Non-radioactive materials were calcined in a box furnace.

The calcined powders were then treated by wet ball milling (water) for 16 hours with 10 mm diameter yttria stabilised zirconia media in rubber lined jars. The milled slurry was dried to a powder at 110-120°C in an oven for the non-radioactive materials or on a hot plate for the Pu-doped materials.

3.2 Oxide-Route Wet-milled Powder Preparation

The oxide precursors were made as follows. The chemicals (Table 3) were weighed out and mixed together in a plastic jar. The blended powder was placed in an alumina container and calcined for 1 hour at 750°C in air.

The calcined powders were placed in rubber jars with 10 mm diameter yttria stabilised zirconia media and wet ball milled in water for 16 hours. The milled slurry was dried at 110-120°C in an oven.

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[2] M W A Stewart, E R Vance, R A Day and A Brownscombe, *Interim Report on Task 1.2: Near Equilibrium Processing Requirements*, ANSTO Report No. R99m012, 1 April 1999, Materials Division, ANSTO, Lucas Heights, Australia.

3.4 Analysis

For the Pu-doped samples, two mounts were made. One small sample was cut from the pellet for scanning electron microscopy and a larger section for X-ray diffraction (XRD) analysis. The samples were mounted in resin and polished to a < 1 μm diamond finish.

XRD of the non-radioactive samples was carried out on the outer surface of the pellet, a ground surface of the pellet and a powder sample from the pellet. Scanning electron microscopy (SEM) samples were prepared as per the Pu-doped samples.

Diffractometers used were either a Siemens D500 diffractometer employing Co K-alpha radiation, or a Scintag X1 Advanced Diffractometer System, with Cu K-alpha radiation.

The samples were examined by SEM using either a JEOL JSM6400 or JEOL JSM6300 machine, both of which are fitted with energy dispersive x-ray spectrometry (EDS) instruments for quantitative analysis.

4 Experimental Results and Discussion

4.1 Al-doped Zirconolite

Samples of this material were made via the alkoxide and oxide-routes. The results are discussed below and are summarised in Table 1. XRD patterns are given in Appendix A.

The composition $Ca_{0.5}Gd_{0.5}HfAl_{0.5}Ti_{1.5}O_7$ with 1 wt. % excess TiO_2 was chosen. In this sample charge compensation is achieved by substituting Gd for Ca on the Ca site.

This composition was not single phase when made via the oxide-route. The phases formed when sintering was carried out at 1350°C in air, were 2M zirconolite, hafnium titanate and Hf-doped rutile. After sintering at 1400°C perovskite was also present.

However when this composition was made via the alkoxide-route (sintering at 1350°C for 50 hours) near single phase zirconolite formed except for a small amount of ~ 1-2 vol. % of $HfTiO_4$ (fig. 1, Table 4, Appendix A). A sample of this material has been sent to LLNL.

A composition $CaZrAl_{0.5}Ti_{1.5}Nb_{0.5}O_7$ was also prepared via the alkoxide-route. In this case Nb on the Ti site provides the charge compensation. A pellet of this composition melted at 1450°C and partially melted at 1400°C. The phases formed (by XRD only) were 2M zirconolite plus significant amounts of zirconium titanate and rutile.

Table 4 - EDS analyses of phases (number of cations) found in the Al-doped zirconolite (fig. 1) sintered in air at 1350°C for 50 hours.

Phase	**Pyrochlore**	**$HfTiO_4$**
Element		
oxygen	7	4
Ca	0.48	0.006
Gd	0.47	0.016
Hf	0.93	0.93
Al	0.55	0.06
Ti	1.57	1.01
Total	3.99	2.02

The standard error in these measurements is ~ 1 %

4.2 Mg-doped Zirconolite

Samples of a Mg-doped zirconolite, $Ca_{0.4}Gd_{0.6}HfMg_{0.3}Ti_{1.7}O_7$ with 1 wt. % excess TiO_2, were made via the alkoxide-route. Here, charge compensation was achieved by substituting Gd for Ca on the Ca site. Sintering was carried out at 1350°C for 50 hours in air. The results are discussed below and are summarised in Table 1. XRD patterns are given in Appendix A.

Near single phase zirconolite with a trace of HfO_2 (< 1 vol. %) was made (Fig. 2, Table 5, Appendix A). The EDS results are given in Table 5. A sample of this material has been given to LLNL.

The EDS composition is slightly different to the nominal composition, $Ca_{0.4}Gd_{0.6}HfMg_{0.3}Ti_{1.7}O_7$. The EDS results suggest that while the Mg is predominantly on the Ti site, some of it may be on other sites.

Table 5 - EDS analyses of phases (number of cations) found in the Mg-doped zirconolite (fig. 2) sintered in air at 1350°C for 50 hours.

Phase	Pyrochlore
Element	
oxygen	7
Ca	0.39 – 0.41
Gd	0.53 – 0.56
Hf	0.94 - 0.95
Mg	0.34 – 0.38
Ti	1.75 – 1.77
Total	4.01 - 4.02

The standard error in each measurements is ~ 1 %

4.3 Ta-doped Pyrochlore

Near single phase "nominally" $CaGdTaTiO_7$, with 1 wt. % excess TiO_2 has been made via the oxide-route and a sample (fig. 3, Table 6, Appendix A) has been given to LLNL. The sample is single-phase pyrochlore when sintered at 1500°C for 48 hours in air. At 1400 and 1450°C some minor peaks, either side of the main pyrochlore peak were present in the XRD pattern (Table 1).

Table 6 - EDS analyses of phases (number of cations) found in the Ta-doped pyrochlore sintered in air at 1500°C for 48 hours.

Phase	Pyrochlore*
Element	
oxygen	7
Ca	0.82 – 0.95
Gd	0.90 – 0.95
Ta	0.99 – 1.02
Ti	1.07 – 1.13
Total	3.88 – 3.95

The standard error in each of these measurements is ~ 1 %

* The pyrochlore phase had some variation in composition across the pellet.

pyrochlore structure of the phase of approximate composition Gd_2TiMoO_7 that formed we will attempt to make the end member $Gd_2Mo_2O_7$. However, it should be noted that the published phase diagram for the MoO_2-Mo_2O_3-Gd_2O_3 does not contain this phase[5]; though the diagram does contain $GdMoO_4$ (Mo nominally 5+). There are also phases listed in the JCPDF XRD pattern files $RE_2Mo_2O_7$ (were RE = Sm, Eu and Tm)[6], which partially fit the additional peaks (over $Gd_2Ti_2O_7$[7]) in the XRD pattern.

4.5 Pu-pyrochlore

Near single-phase pyrochlore (Pu12901A) has been produced using the alkoxide-route (see section 3 above) from a batch with a nominal composition of $CaPuTi_2O_7$ plus 4 wt. % excess TiO_2. The results are summarised in Table 1 and SEM pictures are given in figure 4. The compositions of phases detected, as measured by EDS, are given in Table 7. XRD patterns are given in appendix A. The sample was prepared via the alkoxide-route. Sintering was carried out in air at 1490°C for 16 hours. The sample contains < 1 vol. % PuO_2 and < 1 vol. % TiO_2. One intergranular region of ~ 8 x 20 µm was found (this represents << 0.1 % of the volume), that contained some Ca-Al-Ti-silicate glass from processing impurities (elements detected in glass were Si, Al, Na, Fe, Ca, Pu (~ 4 wt. %) and Ti) and a Pu-bearing phase of composition $Ca_{0.98\text{-}0.99}Pu_{0.32\text{-}0.38}Ti_{2.72\text{-}2.77}O_7$.

A near single phase $CaPuTi_2O_7$ sample (Pu12402A) had been previously produced with > 95 % pyrochlore, but it was contaminated with an impurity Ca-Al-Si glass phase. This glass phase contained (Na, Mg, Al, Si, P, Pu (~ 0.4 wt. %), Ca, Ti, Fe, Ni and Cu) and had perovskite and rutile associated with it. This $CaPuTi_2O_7$ sample completely melted at 1550°C and partially melted at 1525°C. A sample was recovered from the 1525°C sinter. The SEM sample was taken from the edge of the pellet. SEM analysis of this sample showed that it consisted mainly of pyrochlore with an outer layer ~ 500µm thick (fig. 5, Table 8). This outer layer contained significant amounts of PuO_2, rutile, perovskite and the impurity alumino-silicate glass phase, which composed ~ 1-2 vol. % of this outer layer. The XRD Pattern of this sintered pellet only contained pyrochlore, which suggested that the XRD and SEM samples were different. Partial melting of the exterior of the pellet may have caused the decomposition of the pyrochlore to perovskite, PuO_2 and rutile. The XRD sample was placed inside the SEM and examined. The radioactivity levels prevented any quantitative analysis. The interior of the pellet still contained the impurity glass, plus pyrochlore and rutile and some PuO_2. It did not have the decomposition region present at the exterior of the pellet. Some "clean" regions composed almost entirely of pyrochlore could be found.

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[5] Chemical System Gd_2O_3-MoO_2-Mo_2O_3, Figure 91-336, *NIST-AcerS Phase Equilibria Diagrams Database*, version 2, Sept. 1995, ISBN 0-944904-93-9.

[6] JCPDF Pattern numbers, 22-1098, 30-1103, 35-0122.

[7] JCPDF Pattern number 23-0259.

Table 7 - EDS analyses of phases (number of cations) found in the $CaPuTi_2O_7$ sample containing > 98 vol. % pyrochlore (Pu12901A), sintered in air at 1490°C for 16 hours.

Phase Element	Pyrochlore	PuO_2	Rutile
oxygen	7	2	2
Ca	0.92-0.94	0.000-0.007	0.005
Pu	0.94-0.96	1.0	0.003
Ti	2.07-2.09		0.995
Total	3.96-3.97	1.00	1.003

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

The standard error in each of these measurements is ~ 1 %

Table 8 - EDS analyses of phases (number of cations) found in the glass impurity-contaminated Pu-doped pyrochlore (Pu12402A) sintered in air at 1525°C for 16 hours.

Phase Element	Pyrochlore	Rutile	PuO_2	Perovskite
oxygen	7	2	2	3
Ca	0.94-0.98	0.001		0.87-0.90
Pu	0.94-0.96	0.000 - 0.001	1.00	0.05-0.07
Ti	2.05-2.08	1.00		0.99-1.00
Total	3.97-3.99	1.00	1.00	1.93

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

The standard error in these measurements is ~ 1 %

4.6 Pu-brannerite

The results on Pu-brannerite have been summarised in Table 1. The preparation routes are given in section 3 above. The alkoxide-route was used. XRD patterns are given in Appendix A. The following compositions have been made:

- $PuTi_2O_6$ (Pu82)
- $PuTi_2O_6$ with ~ 3 % excess TiO_2 (Pu126)
- $PuTi_2O_6$ with ~ 20 % excess TiO_2 (Pu125)

The first sample (Pu08201A) was made from a small ~ 1 g alkoxide-route batch left over from earlier ANSTO work. It was sintered in air at 1525°C for 16 hours. The maximum yield of brannerite was ~ 50-60 vol. %. Resintering the pellet at a higher temperature (1550°C) (Pu08202A) increased the yield to ~ 60-70 vol. % (fig. 6, Table 9). The additional batches were made to see if the Pu-brannerite yield could be improved.

Table 9 - EDS analyses of phases (number of cations) found in the Pu-doped brannerite (Pu08202A) sintered in air at 1550°C for 16 hours.

Phase	Brannerite	Rutile	PuO_2
Element			
oxygen	6	2	2
Pu	1.01-1.02	0.001	1.000
Ti	1.98-1.99	0.999	0.000
Total	3.00	1.00	1.00

The standard error in these measurements is ~ 1 %

The excess TiO_2 was added to try to obtain complete reaction of the PuO_2.

A sample (Pu12601A) of the batch with ~ 3 wt. % excess TiO_2 was sintered at 1525°C in air for 16 hours but it melted. A sample (Pu12602A) sintered at 1490°C in air for 16 hours did not appear to melt. XRD analysis indicated that this sample consists on PuO_2, rutile and what we believe to be brannerite (the coarse-grained sample may be orientated as only a few brannerite peaks are present). This sample was examined by scanning electron microscopy and was found to have partially melted (fig. 7). The eutectic contained substantial amounts of PuO_2 and TiO_2. The unmelted regions consisted of $PuTi_2O_6$ and ~ 3 vol. % TiO_2 and ~ 1 vol. % PuO_2. Another sample (Pu12603A) was sintered at 1400°C to avoid melting. This sample (fig. 8) consists of PuO_2 and rutile.

The $PuTi_2O_6$ (Pu125) with 20 wt. % excess TiO_2 was fired at 1550°C and formed a melt (Fig 9, Table 11). The molten section consisted of $PuTi_2O_6$ and TiO_2 and the "unmelted" part contained $PuTi_2O_6$, PuO_2 and TiO_2. The X-ray pattern (Appendix A) consists of PuO_2, TiO_2 and additional peaks that we believe are from $PuTi_2O_6$ with preferred orientation. The sample sintered at 1525°C was similar, but did not exhibit the large crystal growth regions and had large regions of "eutectic" melt (fig. 10, Table 11).

It appears that it is very difficult to make near single phase Pu-brannerite. The maximum yield achieved was ~ 70 vol. %. It would appear that the best yields would be achieved by sintering to just below the melting point. This melting point appears to change with the amount of excess TiO_2. The melting point may also be affected by trace amounts of impurity elements. Heating above the melting point results in the decomposition of the brannerite to its constituent oxides (TiO_2 and PuO_2). Heating significantly below the melting point ~ 50-100°C results in low or zero Pu-brannerite yield. An alternative approach would be to dope the brannerite with trace amounts (determined from the Task 1.2 results) of Gd, Ca, U and possibly Th to improve the reactivity.

Table 10 - EDS analyses of phases (number of cations) found in the Pu-doped brannerite (Pu12501A) sintered in air at 1550°C for 16 hours.

Phase	Brannerite	Rutile	PuO_2
Element			
oxygen	6	2	2
Pu	0.99 - 1.01	0.001	1.00
Ti	1.98 – 2.00	0.999	0.00
Total	3.00	1.00	1.00

The standard error in these measurements is ~ 1 %

Table 11 - EDS analyses of phases (number of cations) found in the Pu-doped brannerite (Pu12502A) sintered in air at 1525°C for 16 hours.

Phase	Brannerite	Rutile	PuO_2
Element			
oxygen	6	2	2
Pu	0.996	0.001	1.00
Ti	2.00	0.999	
Total	3.00	1.00	1.00

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

The standard error in these measurements is ~ 1 %

4.7 4M Zirconolites

Samples of the 4M zirconolites from the Task 1.3 work[8]; $Ca_{0.6}Gd_{0.8}Hf_{0.6}Ti_2O_7$ (mws980423 and mws99-0479) and $Ca_{0.7}Gd_{0.6}Hf_{0.7}Ti_2O_7$ (mws980424 and mws99-0480) have been sent to LLNL. The mws99-0479 and mws99-0480were prepared by sintering at 1500°C in air for 50 hours. XRD patterns indicated that the samples were the same as those of mws980423 and mws980424 (Appendix A). These samples were prepared via the alkoxide-route.

The samples are composed of 4M zirconolite and Hf-doped rutile ~ 3 vol. % (figs. 11 and 12, Table 12).

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[8] M W A Stewart, E R Vance and R A Day, *Supplement to Interim Report on Task 1.3: Equilibrium Phase Diagrams*, ANSTO Report No. R99m023, 18 April 1999, Materials Division, ANSTO, Lucas Heights, Australia.

Table 12- EDS analyses of phases (number of cations) found in the 4M zirconolite samples.

	mws980423		mws980424	
Phase	**4M Zirconolite**	**Rutile**	**4M Zirconolite**	**Rutile**
Element				
oxygen	7	2	7	2
Ca	0.57		0.68	
Gd	0.80		0.63	
Hf	0.57	0.11	0.66	0.14
Ti	2.05	0.89	2.03	0.86
Total	3.99	1.00	4.00	1.00

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

The standard error in these measurements is ~ 1 %

4.8 Sn-doped Pyrochlore and Zirconolite Update

A review of the results of the Task 1.4 results [2] on the nominally 4+ impurity samples indicated that Sn might not be a zirconolite stabiliser like Zr and Hf, but may be relatively neutral in its partitioning between pyrochlore and zirconolite; it was found that Sn inhabited the Ti sites. It was proposed that the end members of the relevant Sn-doped pyrochlores and zirconolites be examined, namely:

- $Gd_2Sn_2O_7$
- $CaSnTi_2O_7$
- $CaHfSn_2O_7$

A literature search [9,10] revealed that $Gd_2Sn_2O_7$ pyrochlore could be formed and that:

> "The XRD pattern of $CaZrSn_2O_7$ was very similar to that of $CaHfTi_2O_7$." -(from reference in footnote 4).

$CaSnTi_2O_7$ was found not to make a pyrochlore, but the products were not given [4].

It was decided to study $CaSnTi_2O_7$ and $CaHfSn_2O_7$ compositions.

Sn-doped pyrochlores and/or end member $CaSnTi_2O_7$ and $CaHfSn_2O_7$ compositions were been prepared via the alkoxide-route sintered in air at temperatures between 1450 and 1525°C for the former and 1450 and 1600°C for the latter.

The $CaSnTi_2O_7$ composition was sintered at 1450, 1475, 1500 and 1525°C. It melted at 1525°C.

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[9] R.A. McCauley and F.A. Hummel, "New Pyrochlores of the Charge-Coupled Type" J. Solid State Chem., 33 99-105 (1980).

[10] R.A. McCauley, "Structural Characteristics of Pyrochlore Formation", J. Appl. Phys., 51 [1] 290-294 (1980).

Figures

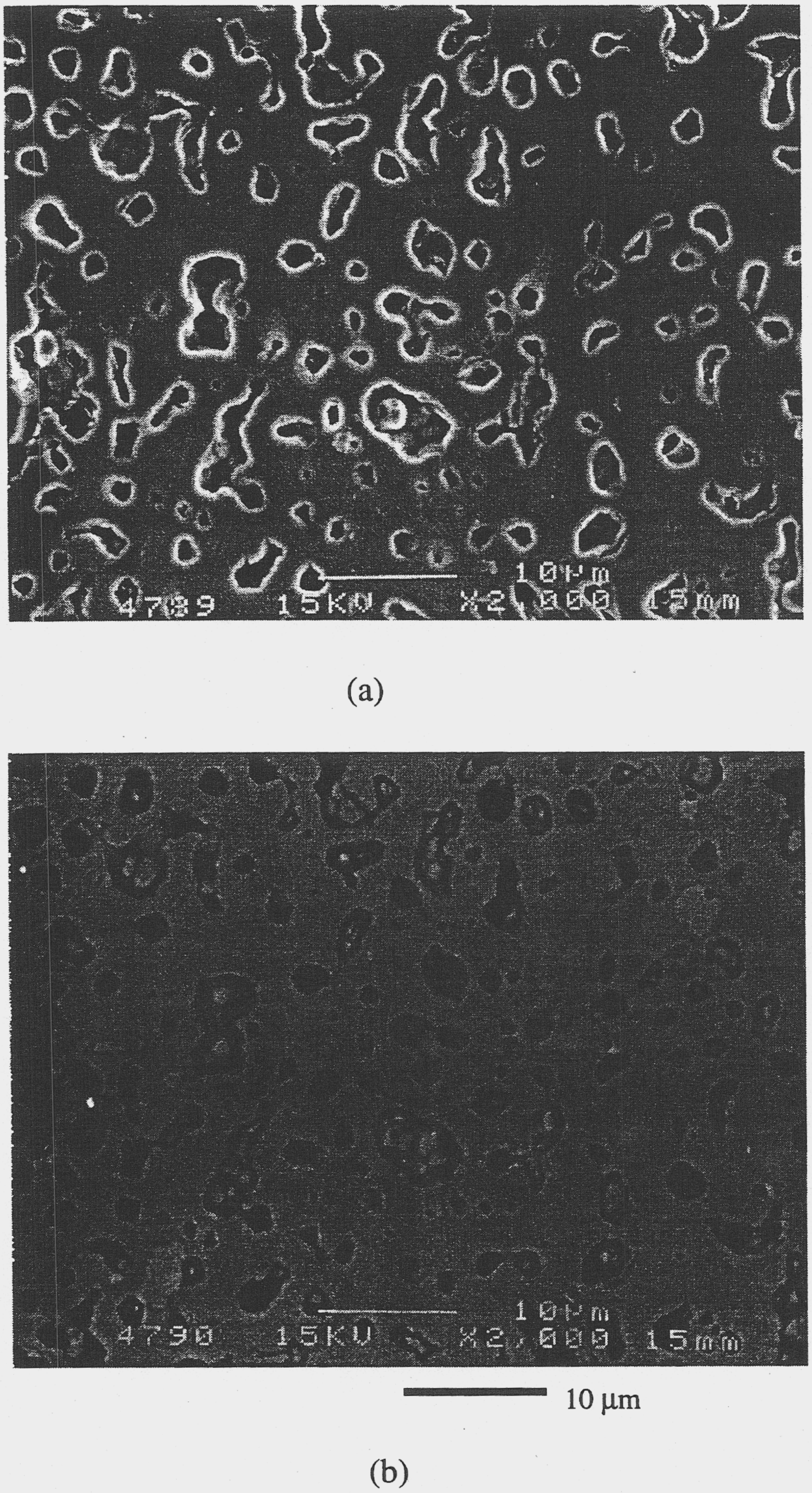


Figure 1: SEM micrographs of the Al-doped zirconolite, $Ca_{0.5}Gd_{0.5}HfTi_{1.5}Al_{0.5}O_7$ sintered at 1350°C for 50 hours in air. (a) Secondary electron micrograph and (b) Backscatter electron micrograph. The sample is near single phase with some porosity (black regions in (b)) and ~ 2 vol. % $HfTiO_4$ (light-grey grains in (b)).

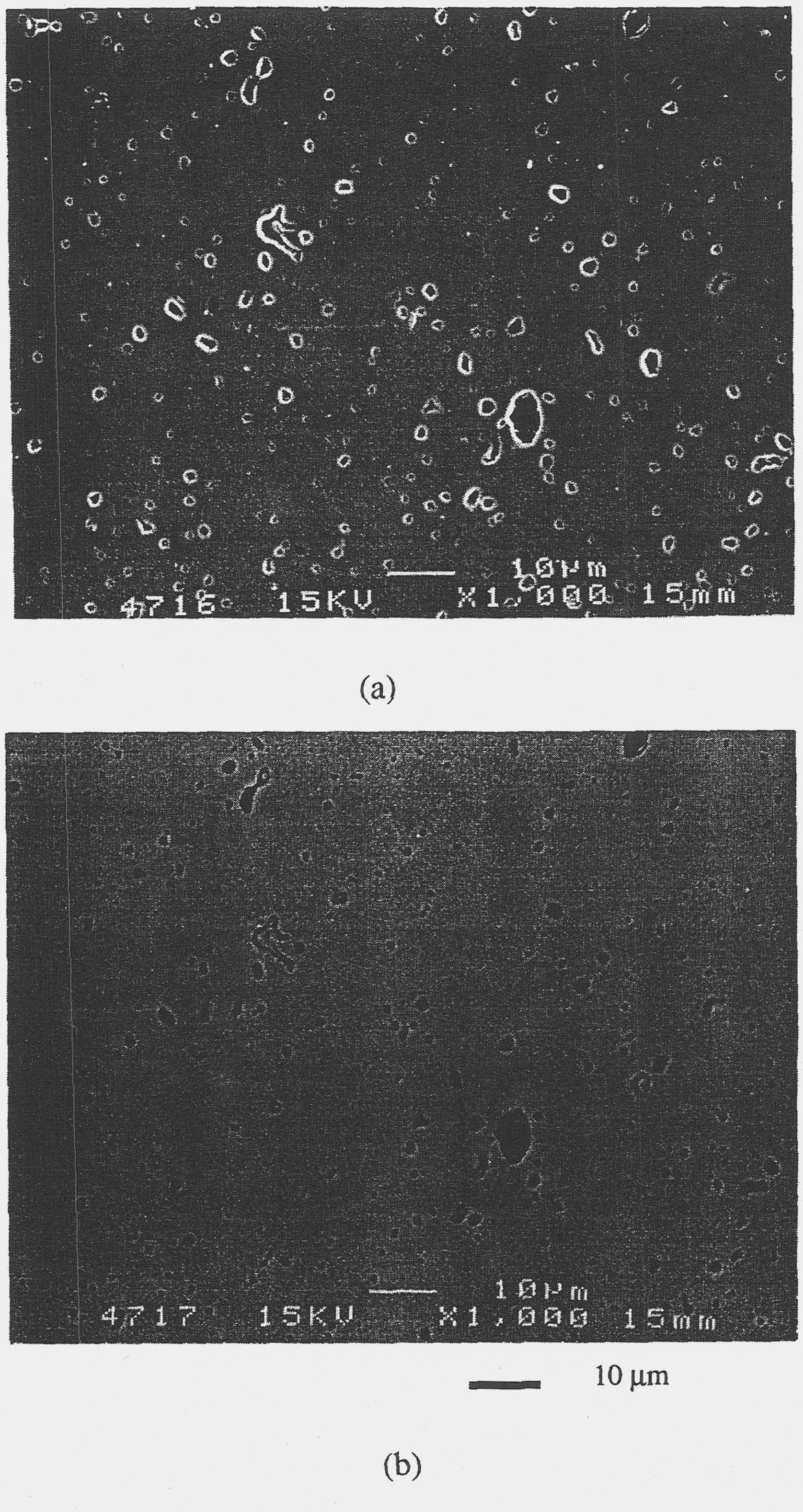
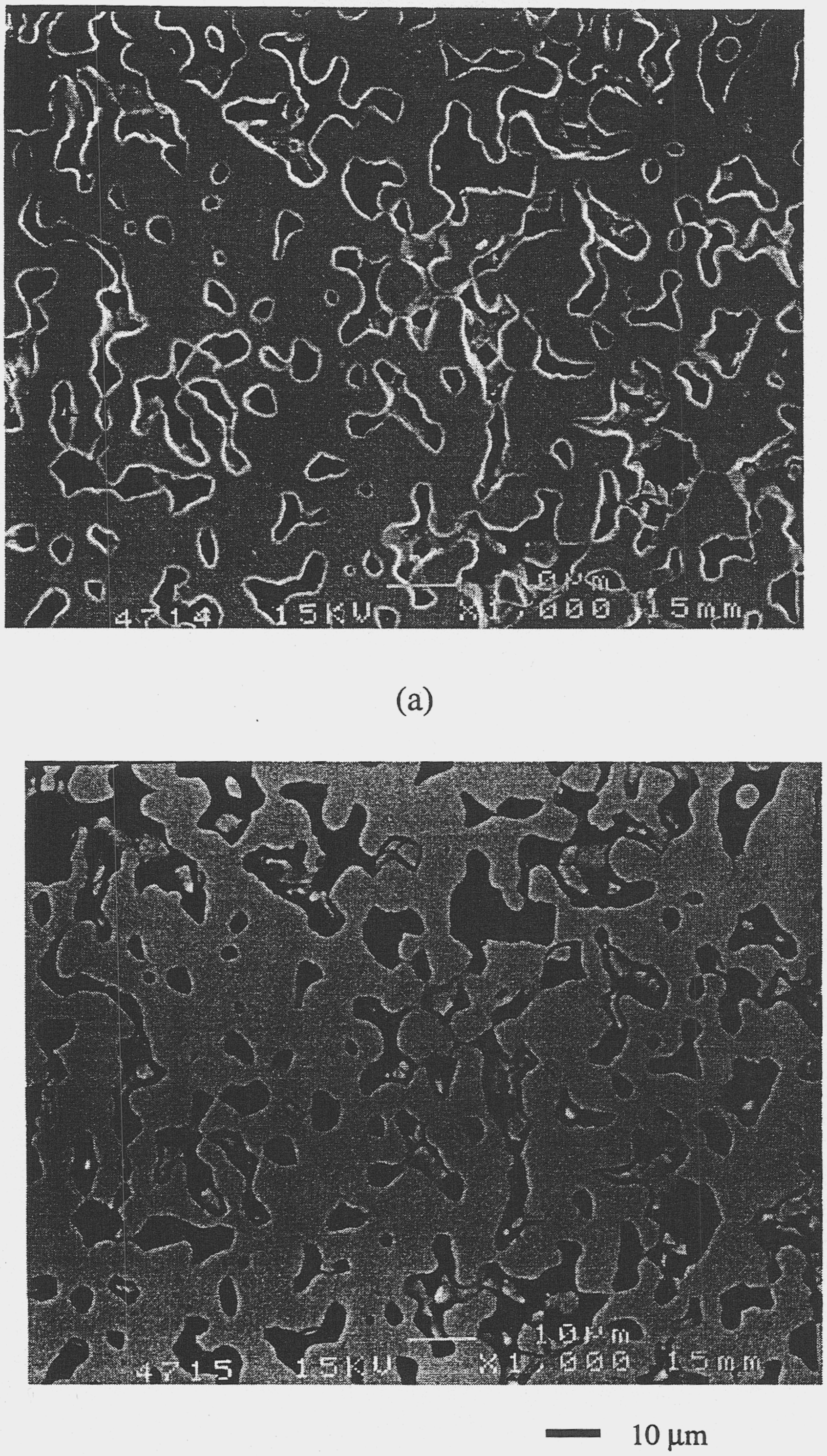


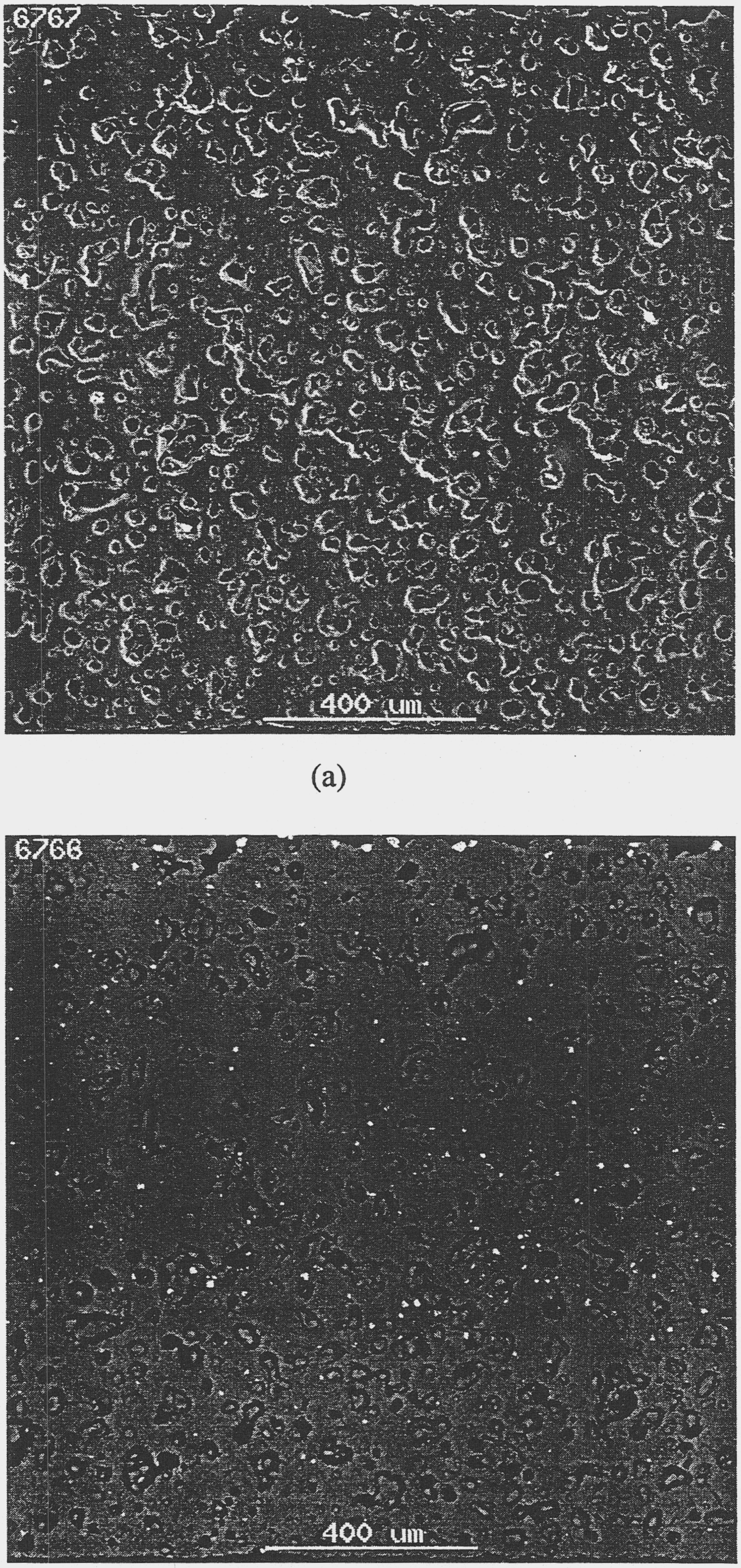
Figure 2: SEM micrographs of the Mg-doped zirconolite, $Ca_{0.4}Gd_{0.6}HfTi_{1.7}Mg_{0.3}O_7$ sintered at 1350°C for 50 hours in air. (a) Secondary electron micrograph and (b) Backscatter electron micrograph. The sample is near single phase with some porosity (black regions in (b)) and a few grains of $HfTiO_4$ (light spots in (b)).



(a)

(b)

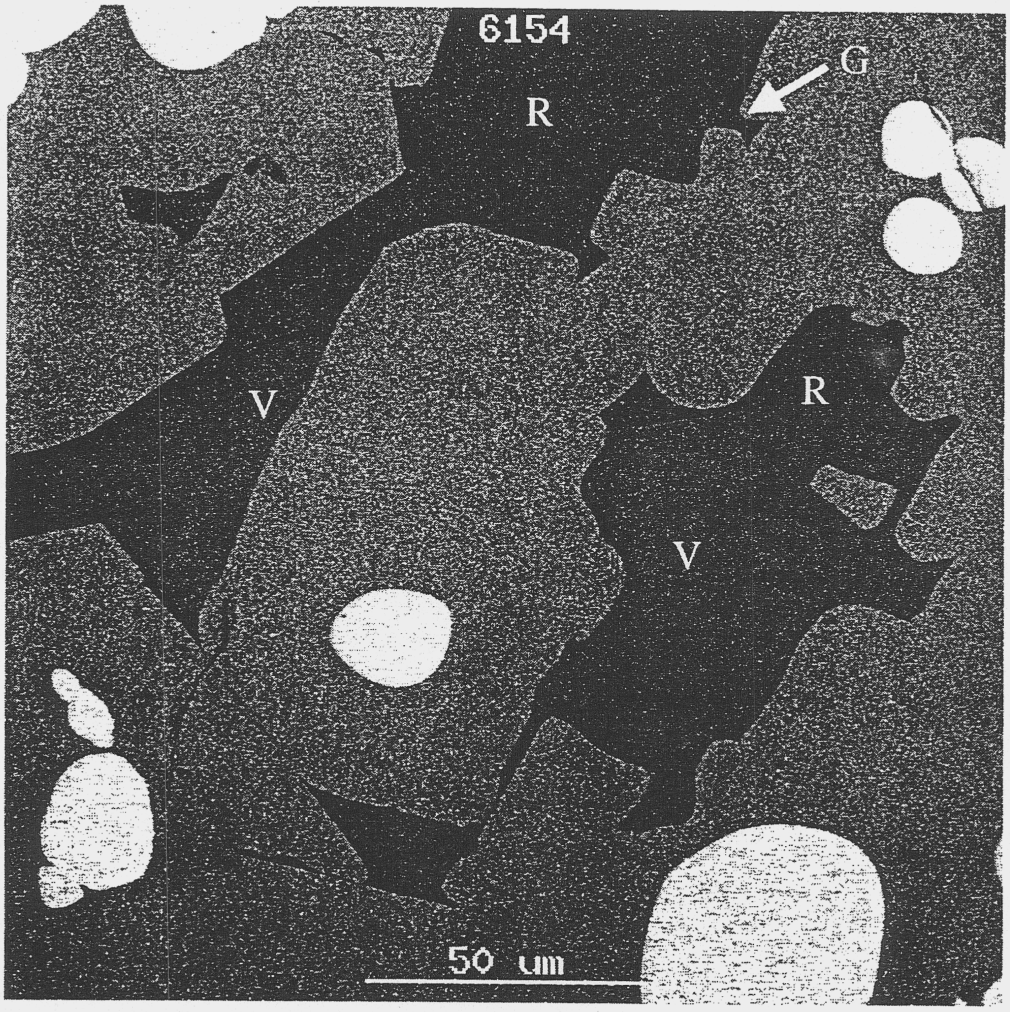
Figure 3. SEM micrographs of the Ta-doped pyrochlore, $CaGdHfTiTaO_7$ sintered at 1500°C for 48 hours in air. (a) Secondary electron micrograph and (b) Backscatter electron micrograph. The sample is single-phase pyrochlore with some porosity (black regions in (b)).



(a)

(b)

Figure 4: see caption overleaf.



(b)

Figure 5: continued

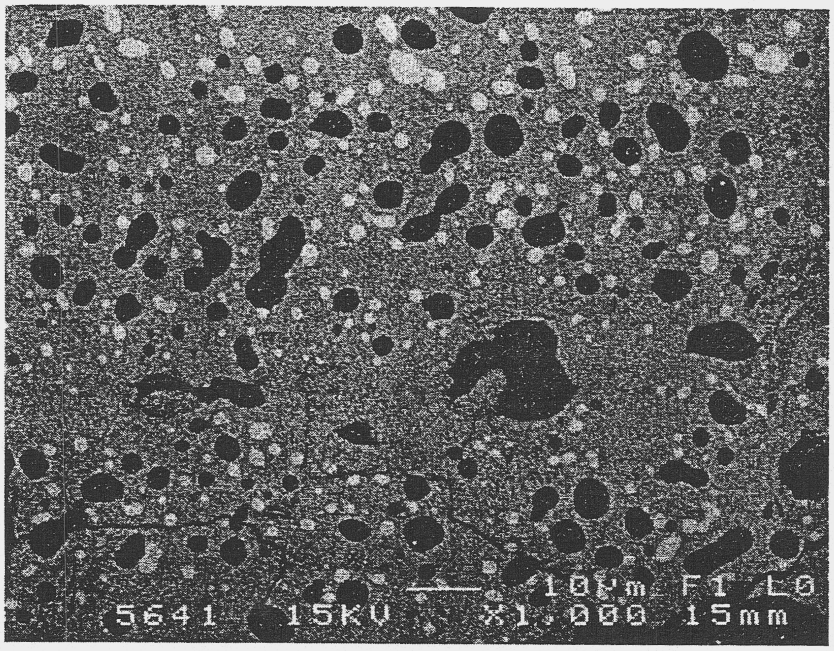


Figure 6: SEM Backscatter electron micrograph of the Pu-brannerite $PuTi_2O_6$ (Pu08202A) sintered at 1550°C for 16 hours in air. The matrix is brannerite, the light grey grains are PuO_2 and the dark grey grains are rutile.

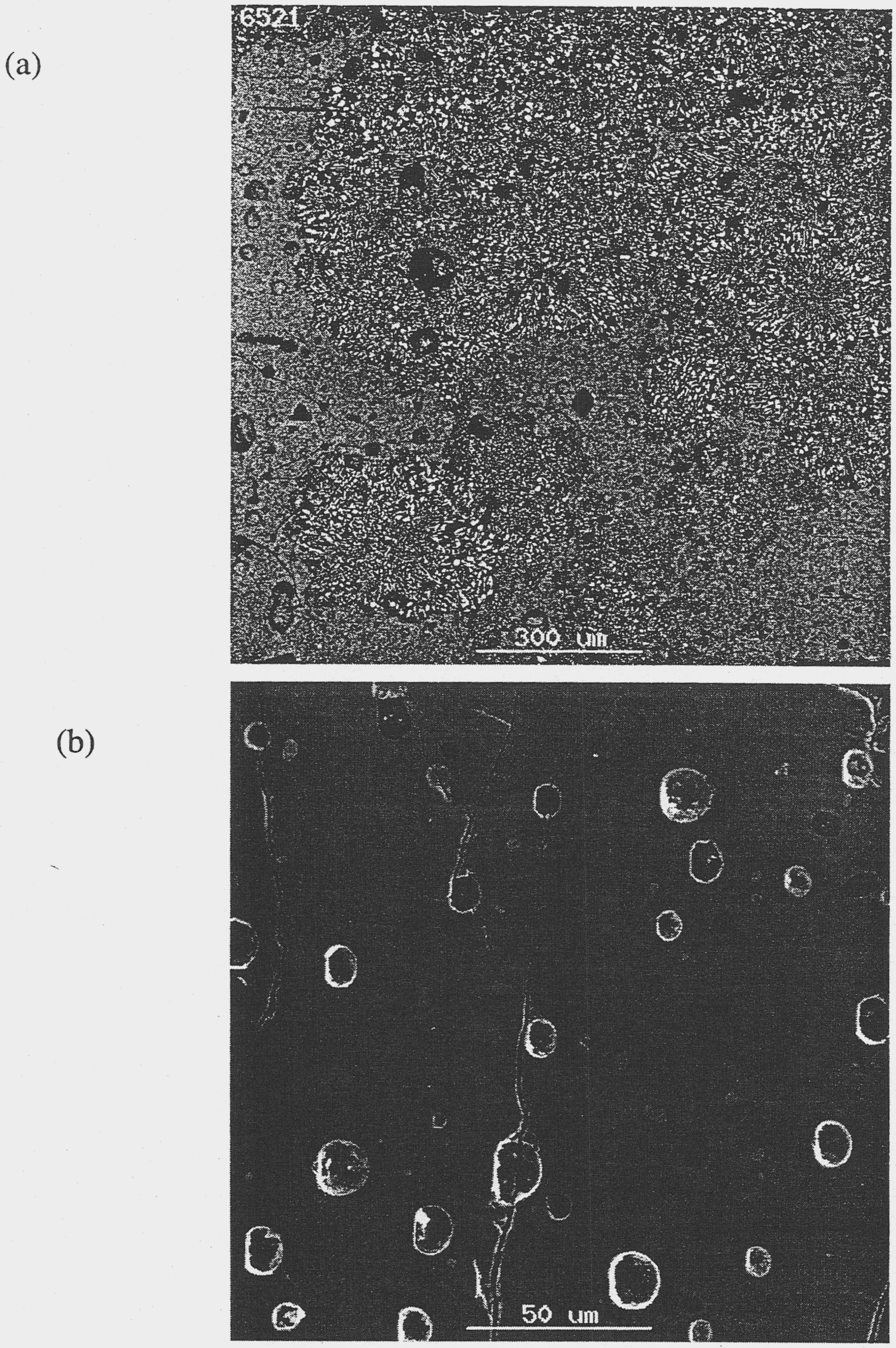


Figure 7: SEM Backscatter electron micrographs of the Pu-brannerite $PuTi_2O_6$ (Pu12602A) sintered at 1490°C for 16 hours in air. The matrix is brannerite, the light grey grains are PuO_2 and the dark grey grains are rutile. (a) A low magnification image showing the "eutectic" regions in which the brannerite appears to have decomposed to PuO_2 and rutile. (b) The "unmelted" region, which is near single phase Pu-brannerite with ~ 1-2 vol. % PuO_2 and 3-5 vol. % rutile.

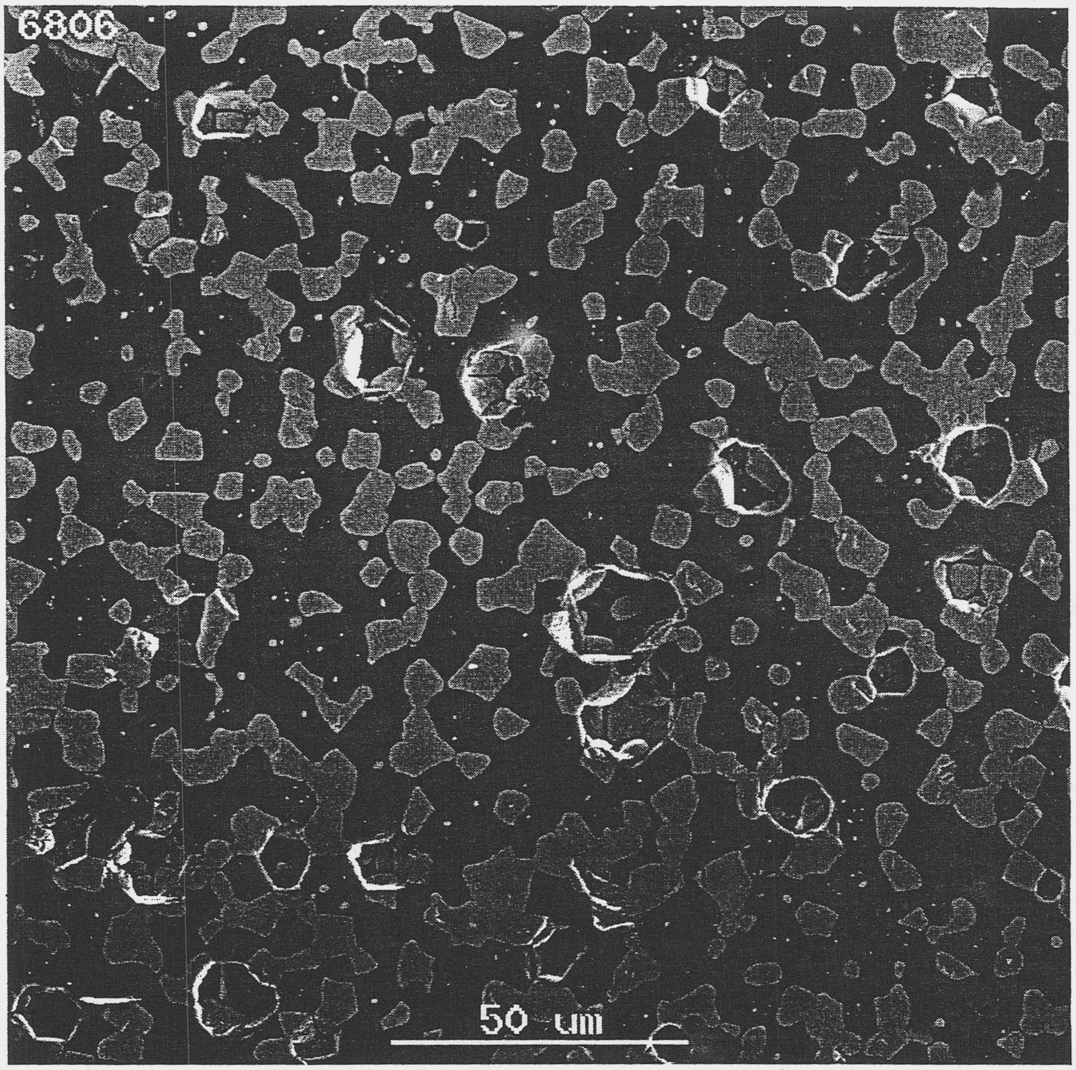


Figure 8: SEM Backscatter electron micrographs of the Pu-brannerite $PuTi_2O_6$ sample (Pu12602A) sintered at 1400°C for 16 hours in air. The yield of brannerite is zero. The sample is composed of PuO_2 (light-grey phase) and TiO_2 (dark-grey phase).

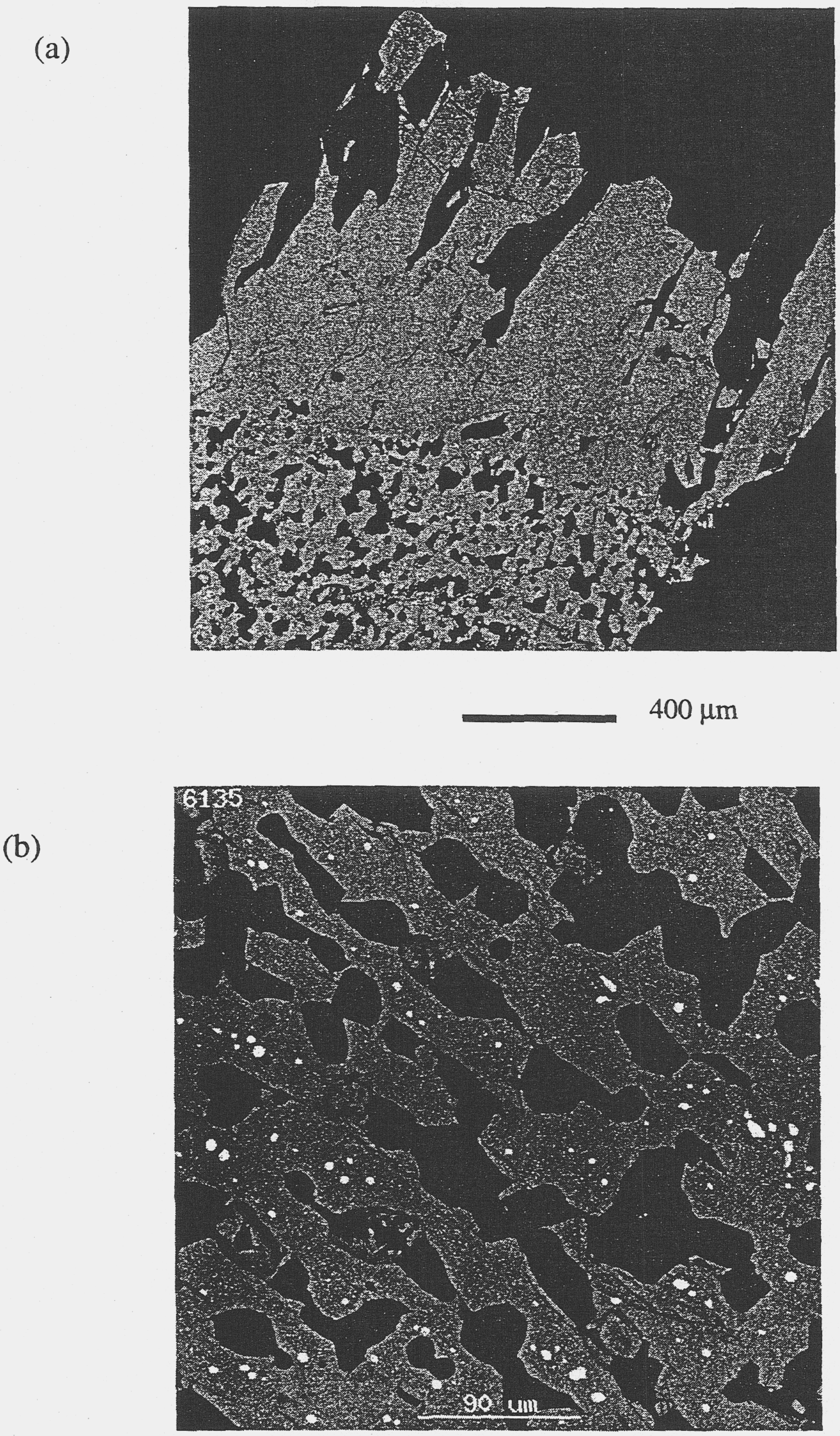
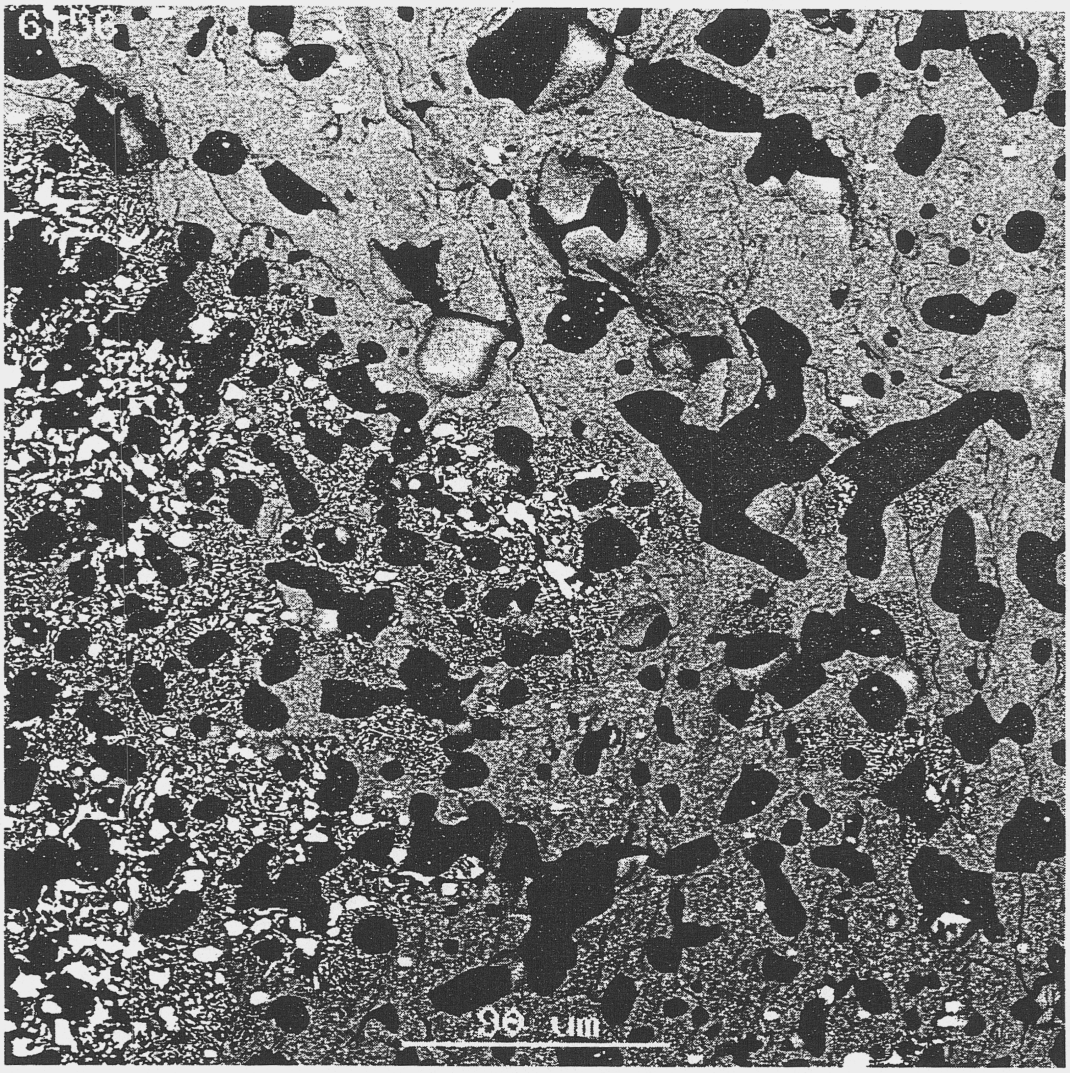


Figure 9: SEM Backscatter electron micrographs of the Pu-brannerite, $PuTi_2O_6$, (Pu12501A) sintered at 1550°C for 16 hours in air. (a) A low magnification view of an outer region of the pellet, showing that two regions exist, an inner region with a finer grain size consisting of rutile, PuO_2 and Pu-brannerite, and an outer region with larger elongated grains of brannerite and rutile that is free of PuO_2. (b) Close up of the finer grained inner region showing a matrix of Pu-brannerite (light grey), and rutile (dark-grey) with some PuO_2 (white) and porosity (black).



(a)

Figure 10: SEM Backscatter electron micrographs of the Pu-brannerite, $PuTi_2O_6$, (Pu12502A) sintered at 1525°C for 16 hours in air. (a) A micrograph showing that two regions exist, a brannerite-rich region and a eutectic region. (b) The brannerite-rich region that also contains some PuO_2 (white) and rutile (dark-grey). (c) Eutectic region of Pu-brannerite (light grey), and rutile (dark-grey) with some PuO_2 (white) and porosity (black).

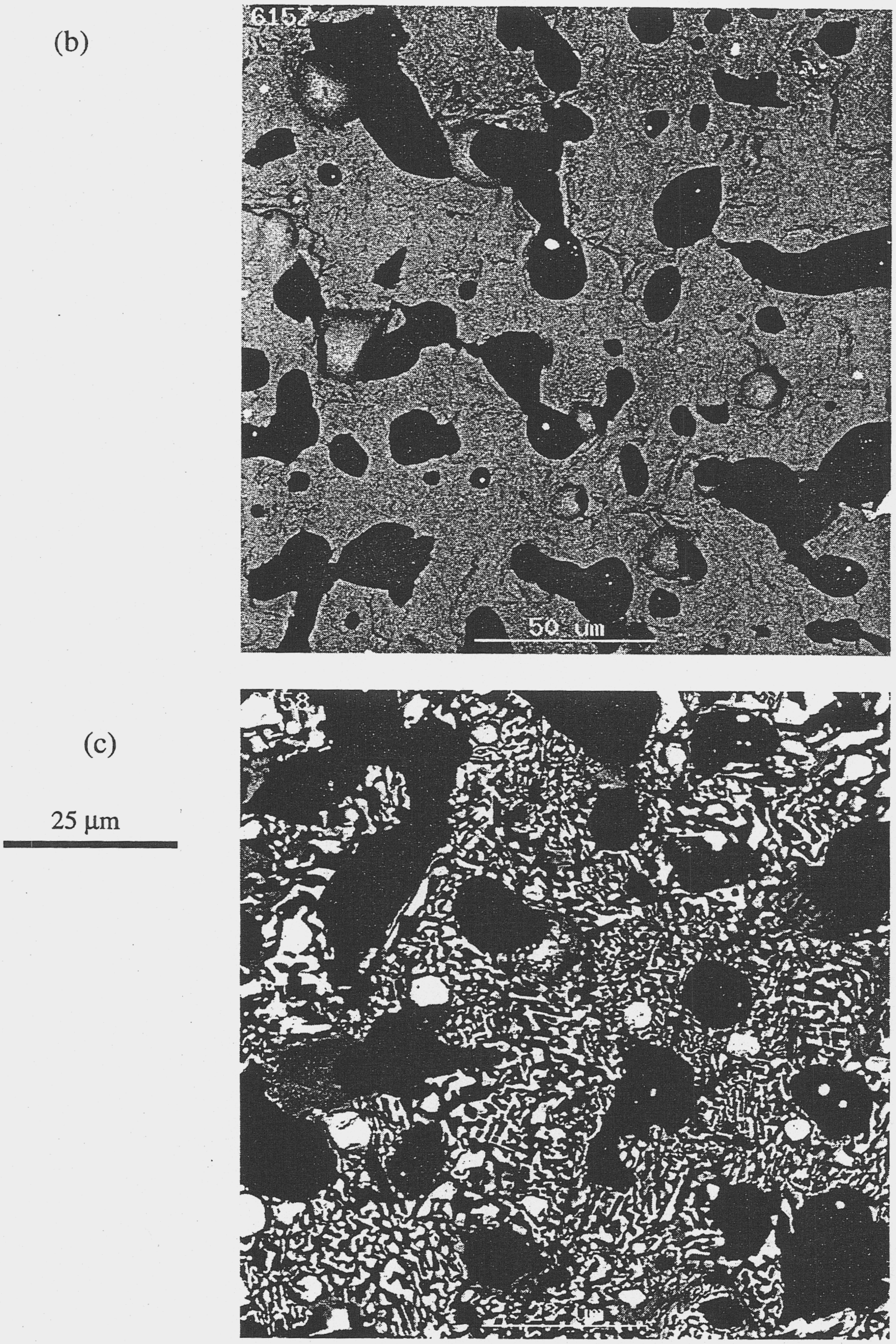


Figure 10: Continued

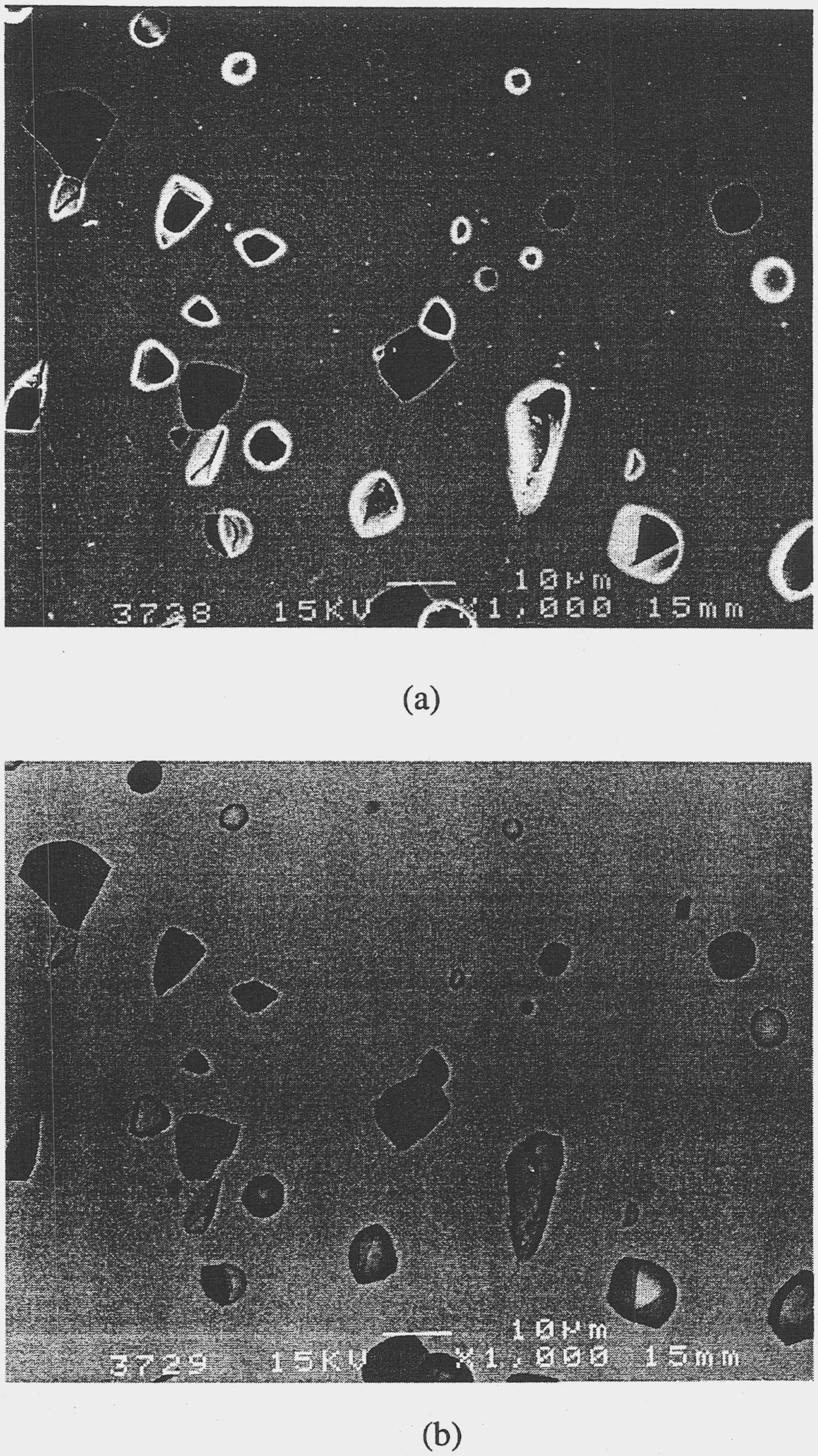
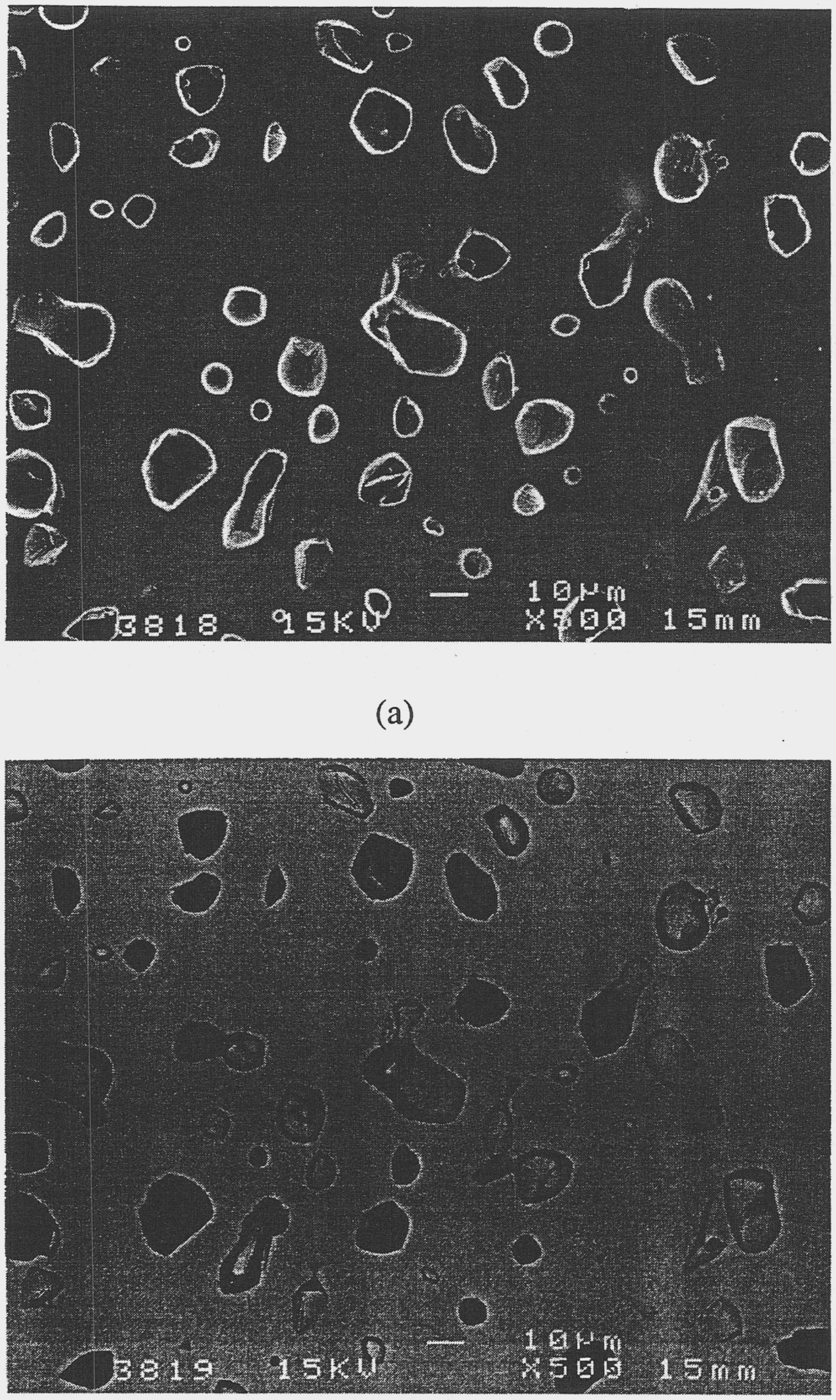


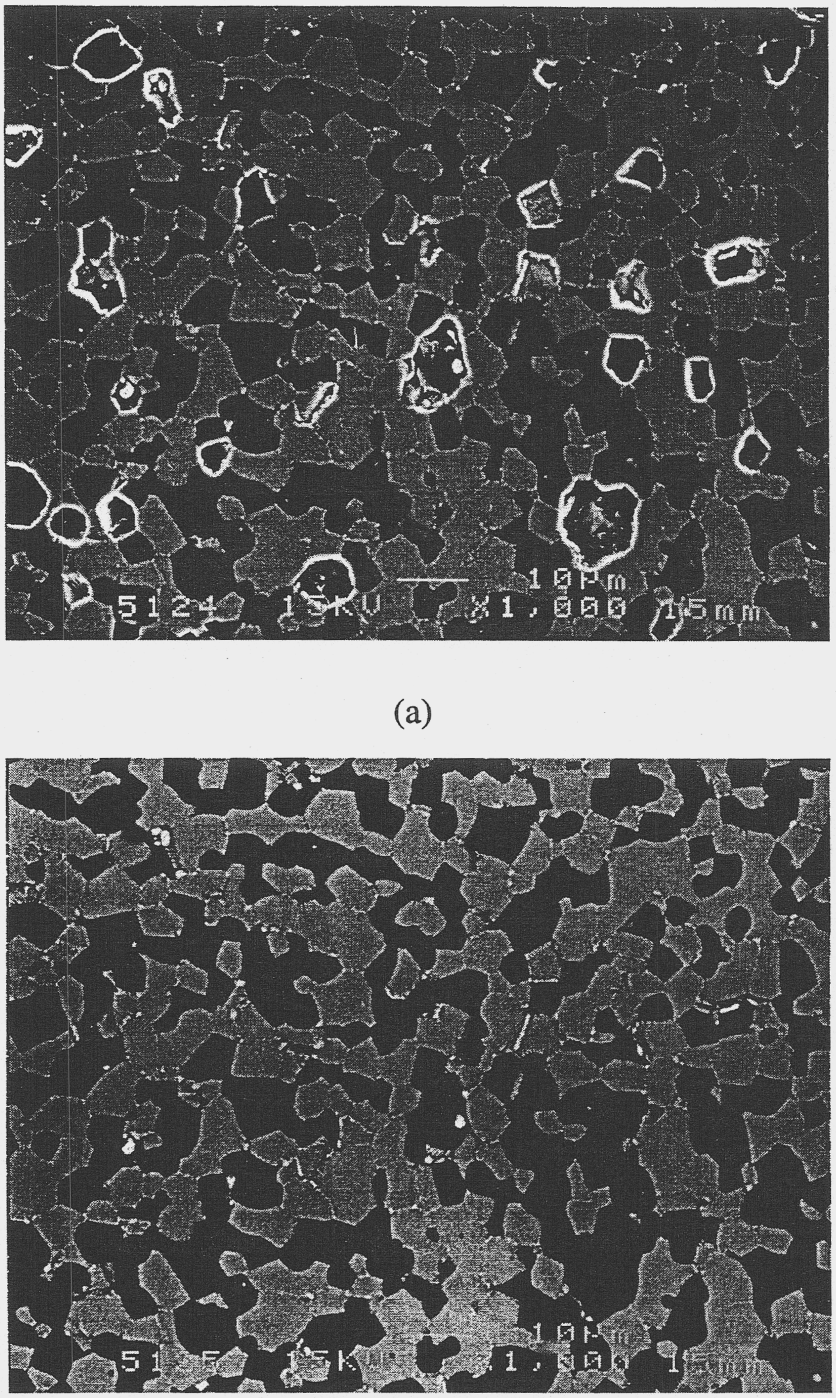
Figure 11: SEM images of mws980423 ($Ca_{0.6}Gd_{0.8}Hf_{0.6}Ti_2O_7$) prepared by sintering at 1500 for 100 hours in air. (a) Secondary electron micrograph and (b) Backscatter electron micrograph. The pellet consists of a 4M zirconolite (matrix), with some Hf-doped rutile (dark-grey) and porosity.



(a)

(b)

Figure 12: SEM images of mws980423 ($Ca_{0.7}Gd_{0.6}Hf_{0.7}Ti_2O_7$) prepared by sintering at 1500°C for 100 hours in air. (a) Secondary electron micrograph and (b) Backscatter electron micrograph. The pellet consists of a 4M zirconolite (matrix), with some Hf-doped rutile (dark-grey) and porosity.



(a)

(b)

Figure 13: SEM images of mws990521 ($CaSnTi_2O_7$) prepared by sintering at 1475°C for 100 hours in air. (a) Secondary electron micrograph and (b) Backscatter electron micrograph. The pellet consists of perovskite (dark-grey), $SnTiO_4$ (grey grains) and Ti-doped SnO_2 (white regions between the $SnTiO_4$ grains.

A Appendix A X-ray Diffraction Results

X-ray diffraction of the non-radioactive samples was carried out on the outer surface of the pellet, a ground surface of the pellet and a powder sample from the pellet. The Pu-doped samples examined by XRD were samples mounted in resin and polished.

Diffractometers used were:

Siemens D500 diffractometer employing Co K-alpha radiation. Siemens D500 files are prefixed with a s (s*.raw).

Scintag X1 Advanced Diffractometer System, with Cu K-alpha radiation. Scintag files are prefixed with a t (t*.raw).

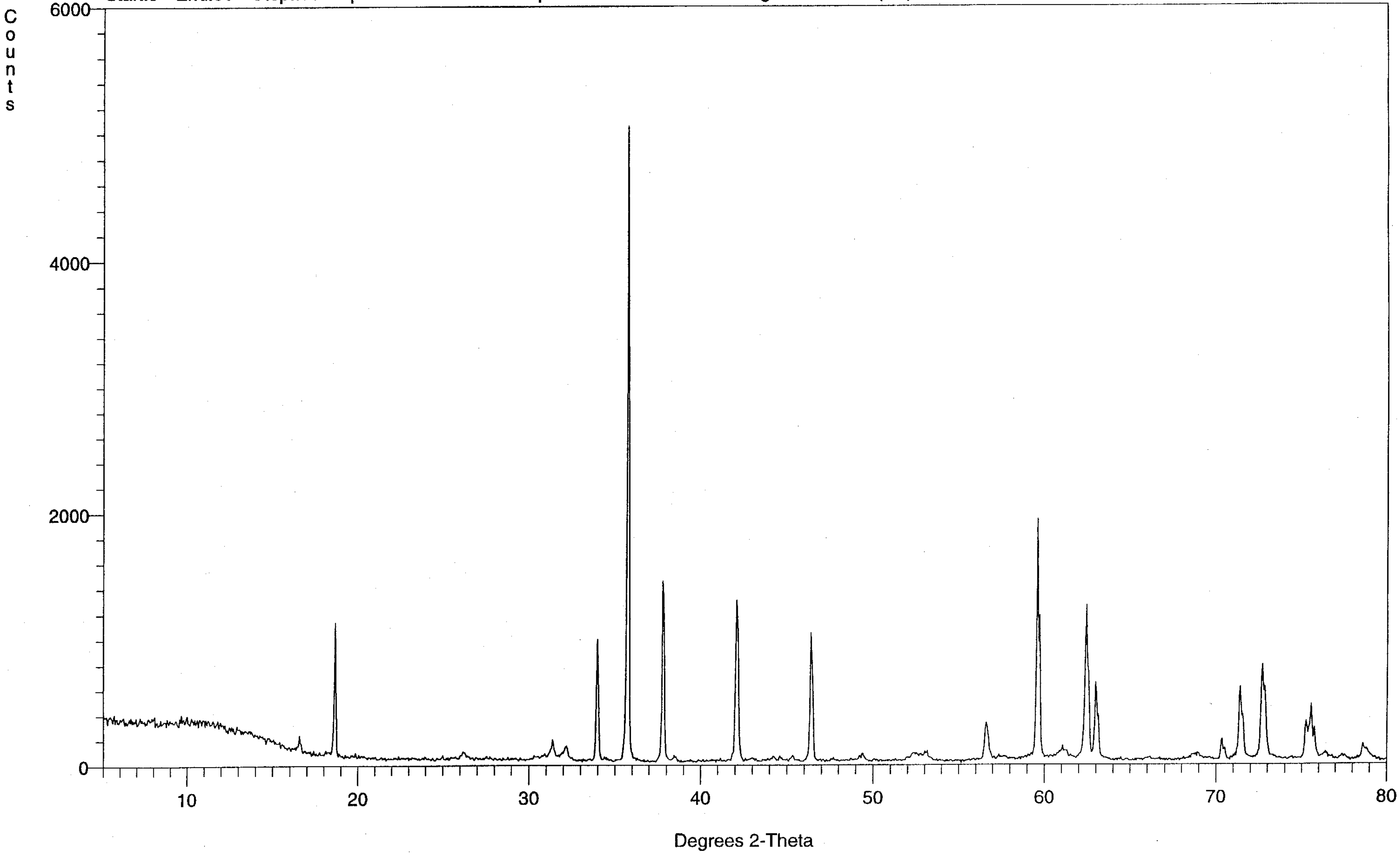
Additional files such as *.txt, or *.cpi of the above raw files have been included when available.

A.1 Al-doped Zirconolite

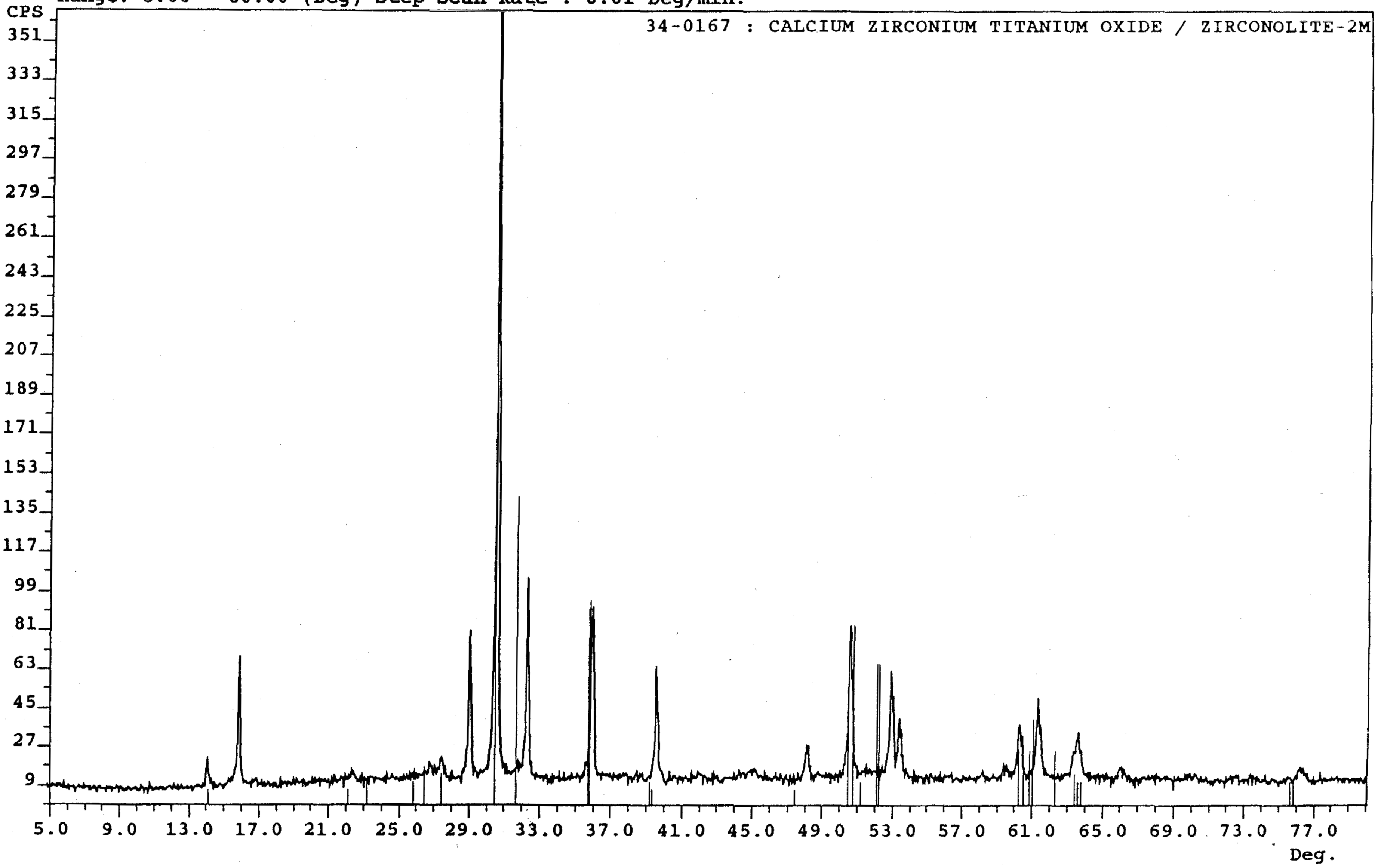
The following Patterns have been sent as files. Print-outs of the data have been placed in this appendix. Patterns taken from mws99-0495 pellet sintered at 1350°C for 50 hours in air.

Surface	s16036
Ground Surface	t1955
Powder	s15688
Powder with tungsten	s15962

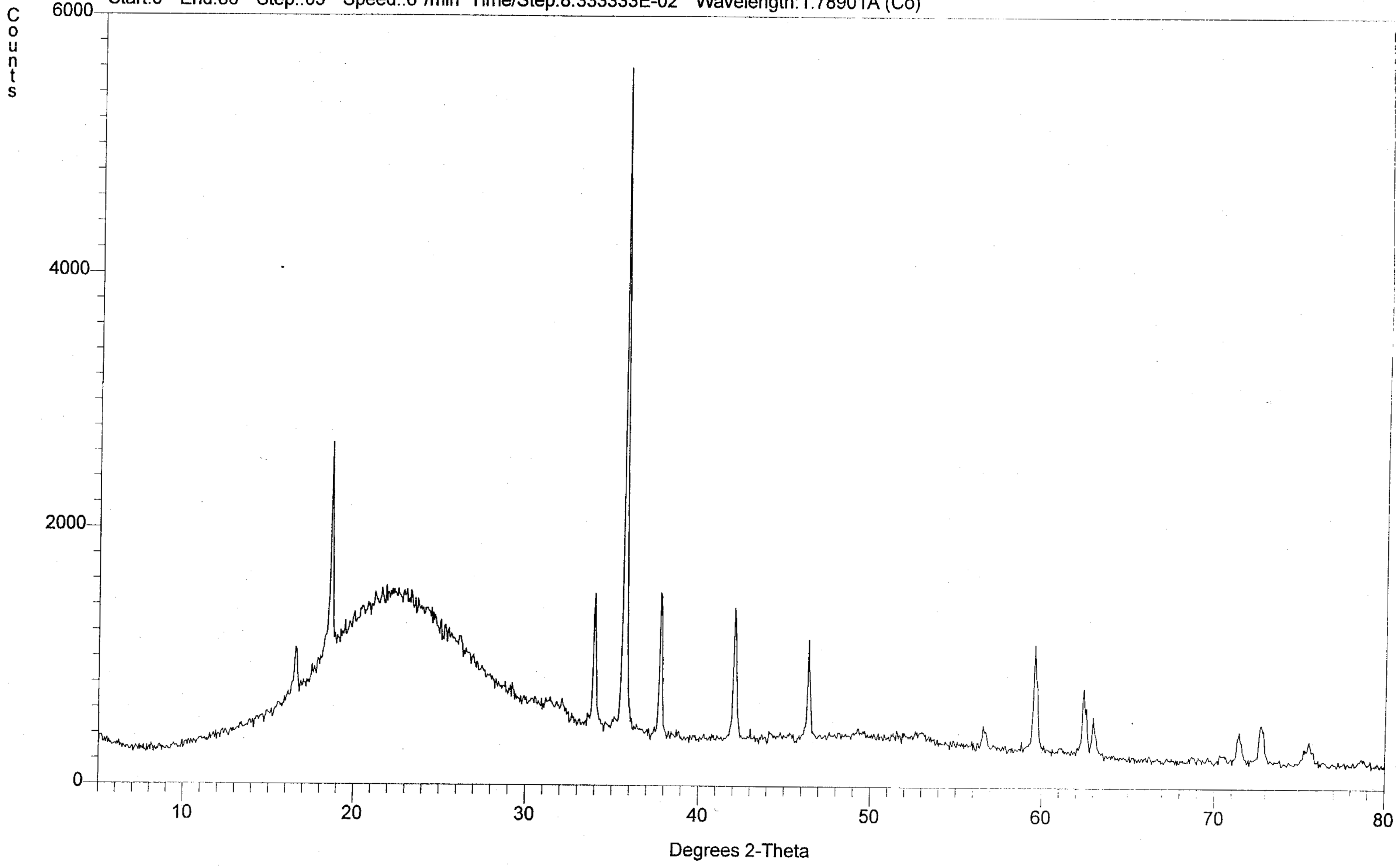
File: e:\data\xrd\s16036.cpi   Date: 11-18-1999   Comment: Al-doped zirconolite pellet surface (mws99-0495).
Start:5° End:80° Step:.05° Speed:.6°/min Time/Step:8.333333E-02° Wavelength:1.78901Å (Co)



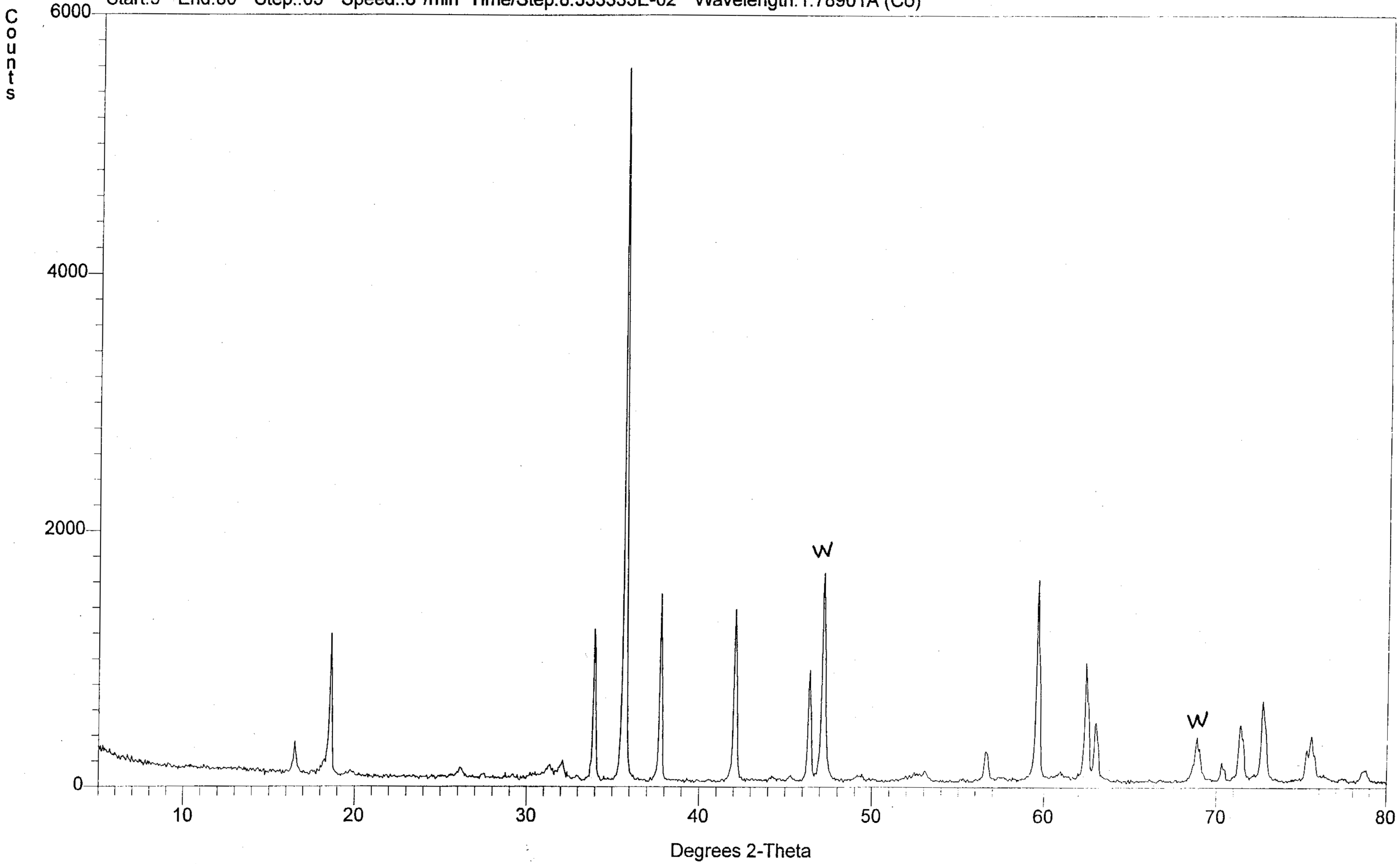
File: t1955, ID: mws99-0495 pellet Al-doped zirconolite surface ground
Date: 07/23/99 20:42 Step : 0.050° Cnt Time: 10.000 Sec.
Range: 5.00 - 80.00 (Deg) Step Scan Rate : 0.01 Deg/min.



File: e:\data\xrd\s15688.cpi Date: 11-17-1999 Comment: Al-doped zirconolite powder (mws99-0495)
Start:5° End:80° Step:.05° Speed:.6°/min Time/Step:8.333333E-02° Wavelength:1.78901Å (Co)



File: e:\data\xrd\s15962.cpi Date: 11-17-1999 Comment: Al-doped zirconolite powder with W metal standard (mws99-0495)
Start:5° End:80° Step:.05° Speed:.6°/min Time/Step:8.333333E-02° Wavelength:1.78901Å (Co)

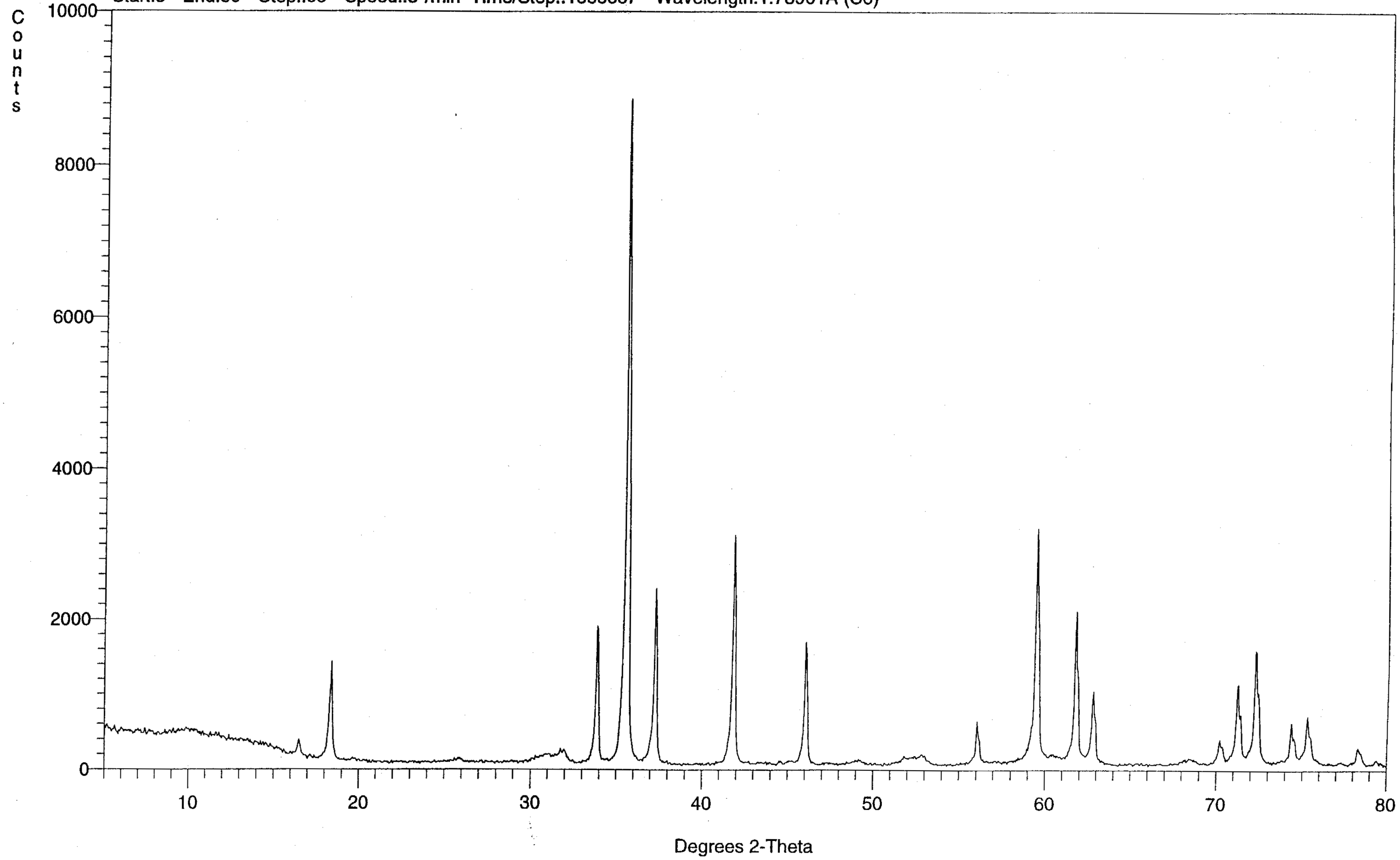


A.2 Mg-doped Zirconolite

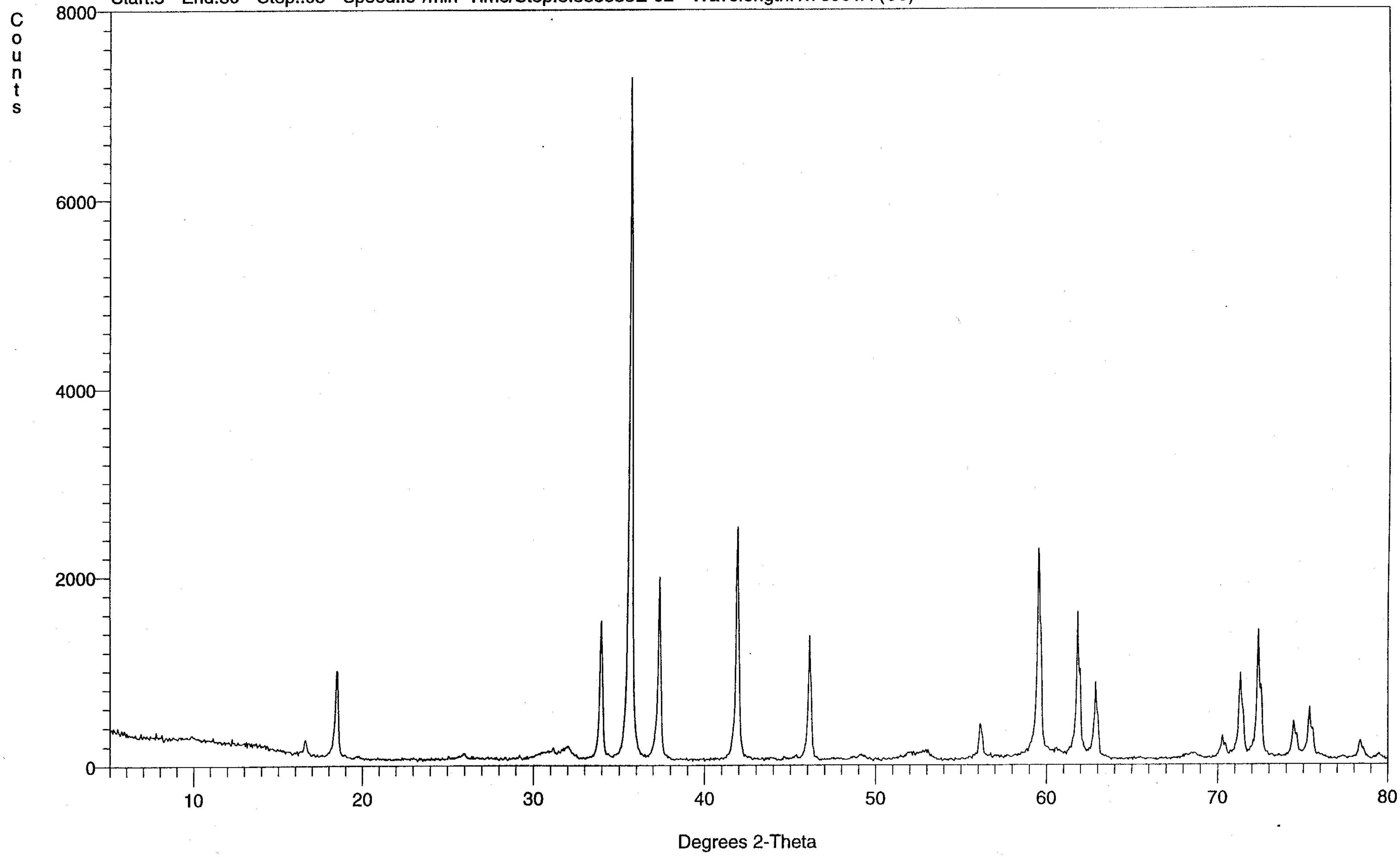
The following Patterns have been sent as files. Print-outs of the data have been placed in this appendix. Patterns taken from mws99-0491 and mws99-0486 pellets both of which were sintered at 1350°C for 50 hours in air.

Surface	s15628
Ground Surface	s15669
Powder	s15960
Powder with tungsten	s15961

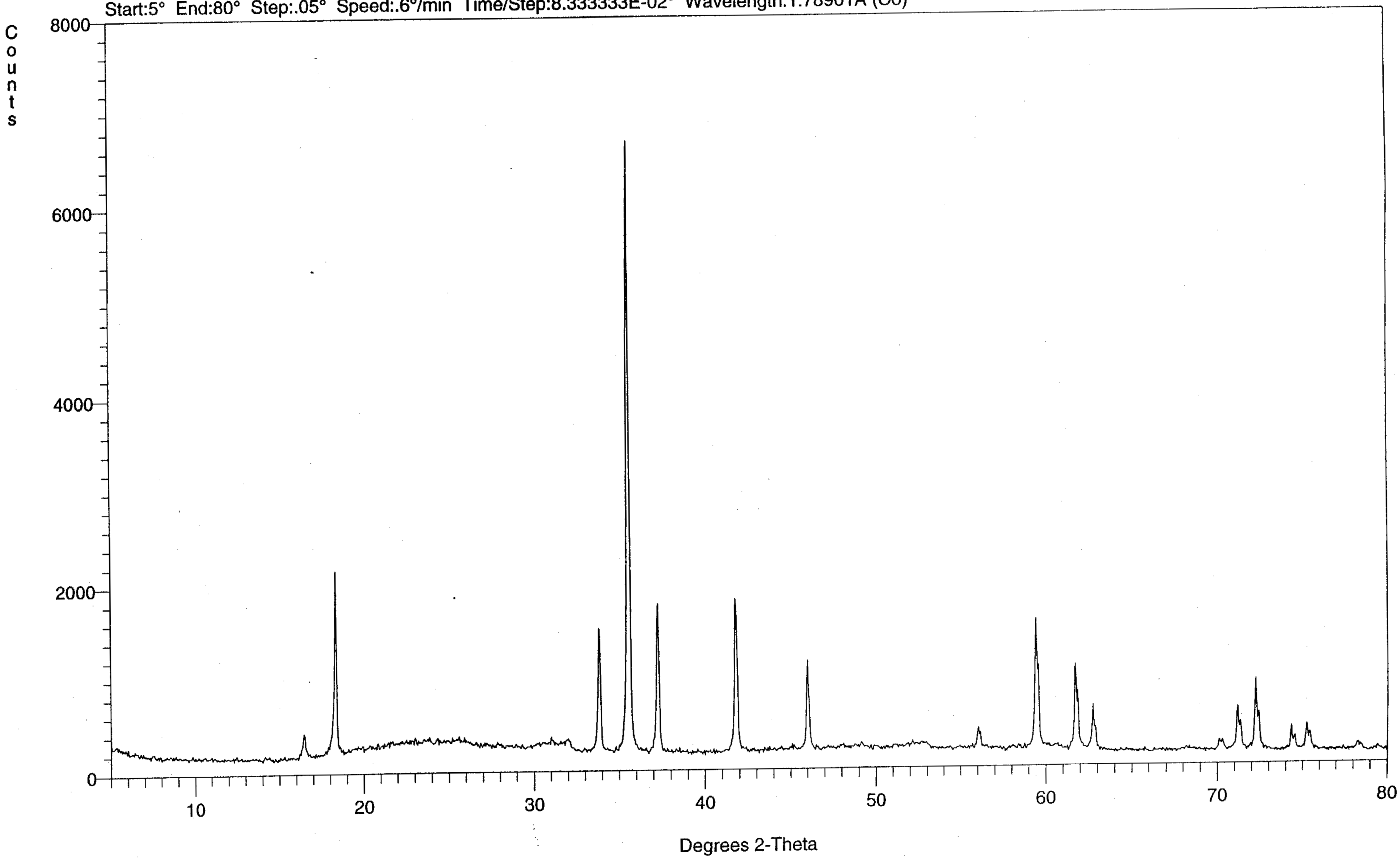
File: e:\data\xrd\s15628.cpi   Date: 11-18-1999   Comment: Mg-doped zirconolite surface (mws99-0486)
Start:5° End:80° Step:.05° Speed:.3°/min Time/Step:.1666667° Wavelength:1.78901Å (Co)



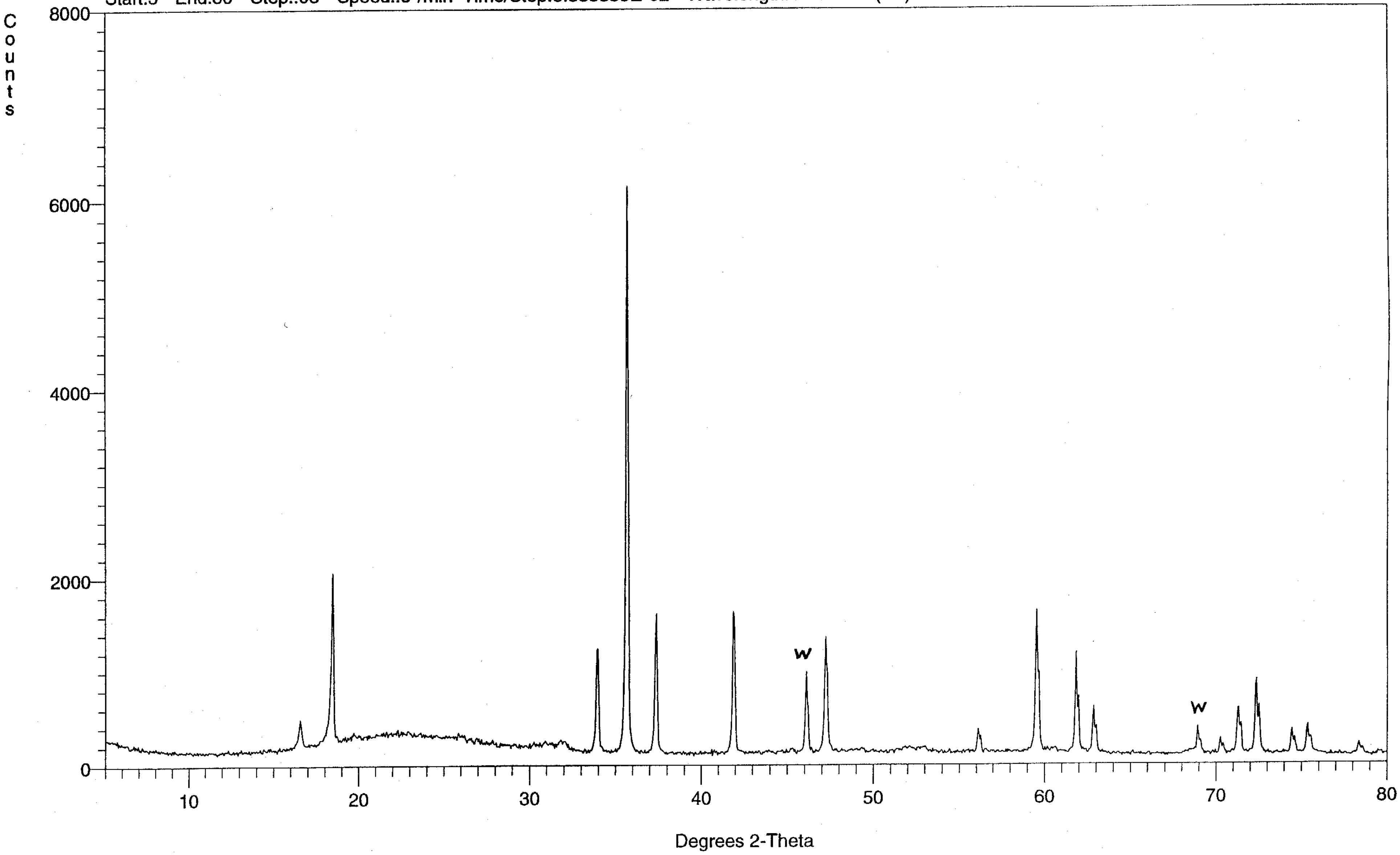
File: e:\data\xrd\s15669.cpi   Date: 11-18-1999   Comment: Mg-doped zirconolite ground surface (MWS99-0491)
Start:5° End:80° Step:.05° Speed:.6°/min Time/Step:8.333333E-02° Wavelength:1.78901Å (Co)



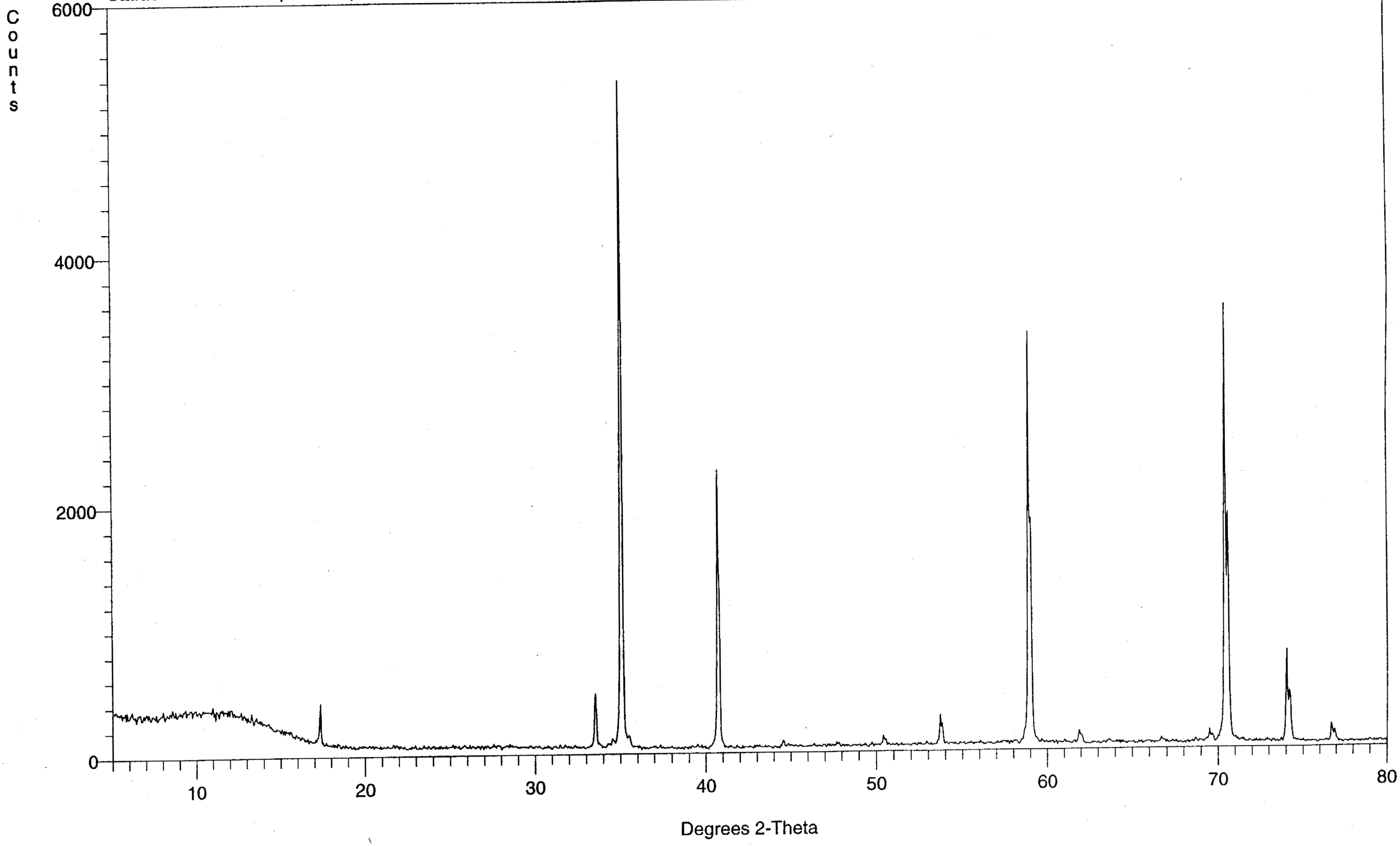
File: e:\data\xrd\s15960.cpi Date: 11-18-1999 Comment: Mg-doped zirconolite powder (mws99-0491)
Start:5° End:80° Step:.05° Speed:.6°/min Time/Step:8.333333E-02° Wavelength:1.78901Å (Co)



File: e:\data\xrd\s15961.cpi   Date: 11-18-1999   Comment: Mg-doped zirconolite powder with W (mws99-0491)
Start:5° End:80° Step:.05° Speed:.6°/min Time/Step:8.333333E-02° Wavelength:1.78901Å (Co)

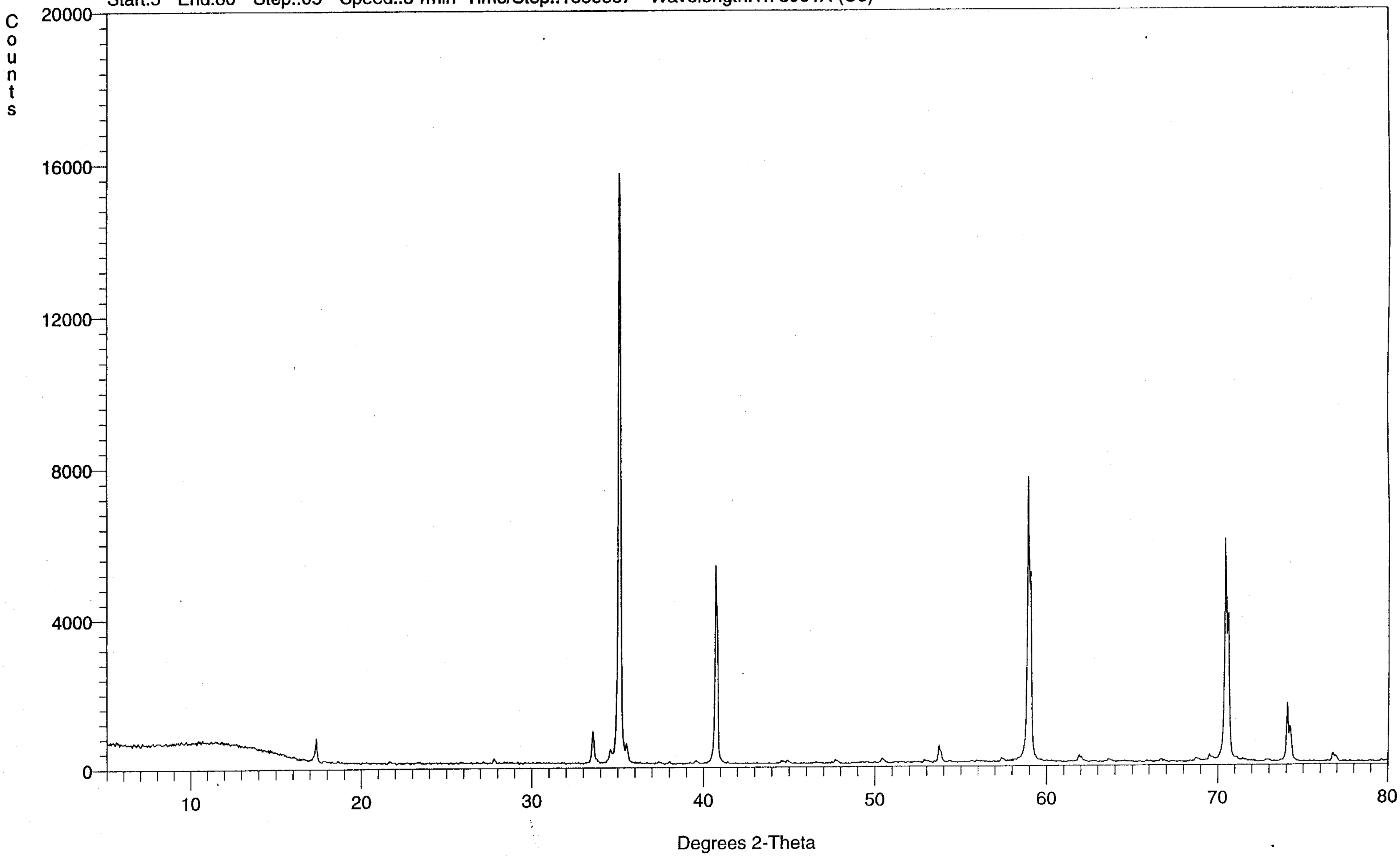


File: e:\data\xrd\s16009.cpi   Date: 11-18-1999   Comment: Ta-doped pyrochlore pellet surface (mws99-0535)
Start:5° End:80° Step:.05° Speed:.6°/min Time/Step:8.333333E-02° Wavelength:1.78901Å (Co)



File: e:\data\xrd\s16012.cpi   Date: 11-18-1999   Comment: Ta-doped pyrochlore pellet ground surface (mws99-0535)

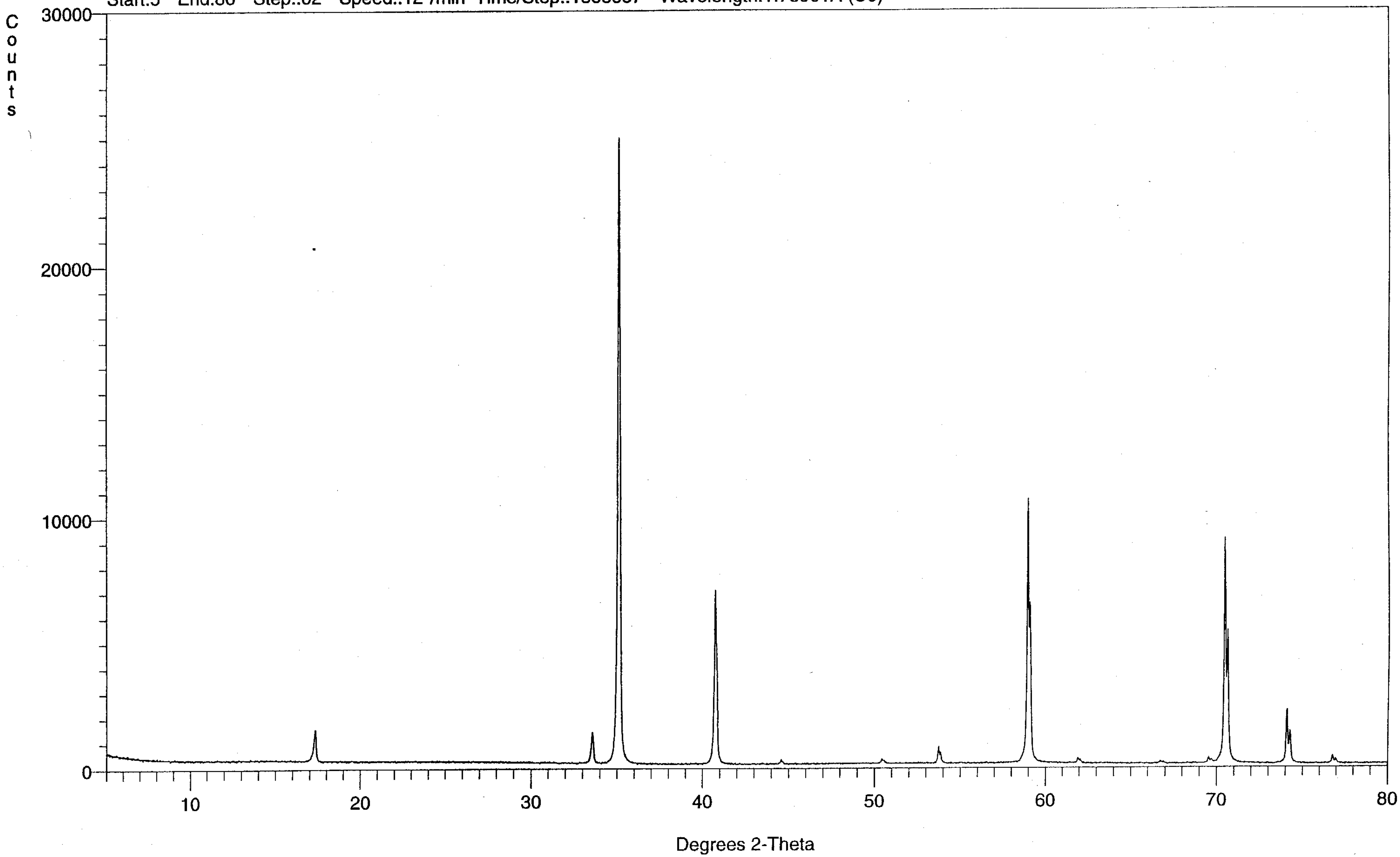
Start:5° End:80° Step:.05° Speed:.3°/min Time/Step:.1666667° Wavelength:1.78901Å (Co)



A.3 Ta-doped Pyrochlore

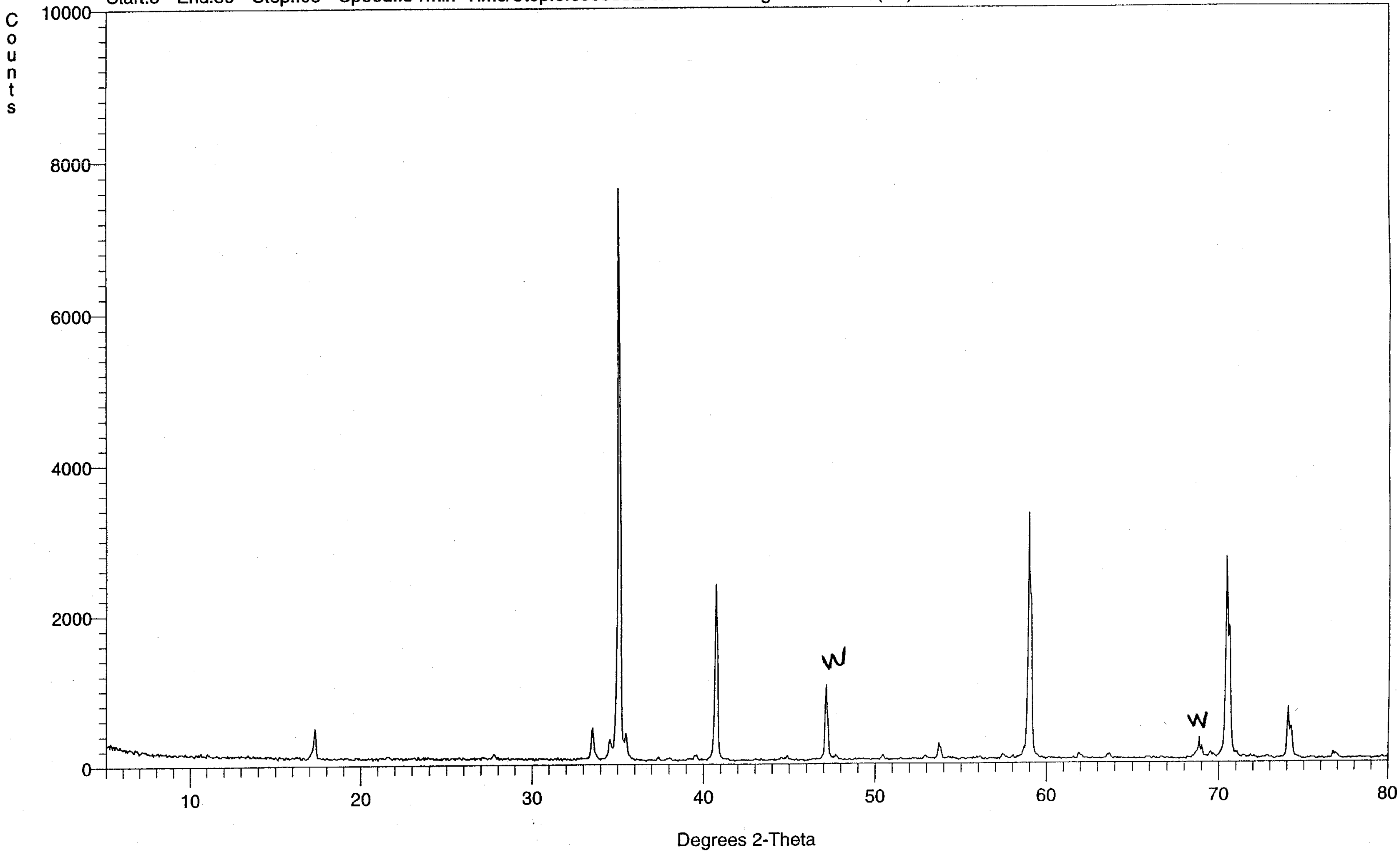
The following Patterns have been sent as files. Print-outs of the data have been placed in this appendix. . Patterns taken from mws99-0477 and mws99-0535 pellets both of which were sintered at 1500°C for 48 hours in air.

• Surface	s16009
• Ground Surface	s16012
• Powder	s15637
• Powder with tungsten	s16037



File: e:\data\xrd\s15637.cpi   Date: 11-18-1999   Comment: Ta-doped pyrochlore powder (mws99-0477)
Start:5° End:80° Step:.02° Speed:.12°/min Time/Step:.1666667° Wavelength:1.78901Å (Co)

File: e:\data\xrd\s16037.cpi Date: 11-18-1999 Comment: Ta-doped pyrochlore powder with W metal standard (mws99-0535).
Start:5° End:80° Step:.05° Speed:.6°/min Time/Step:8.333333E-02° Wavelength:1.78901Å (Co)



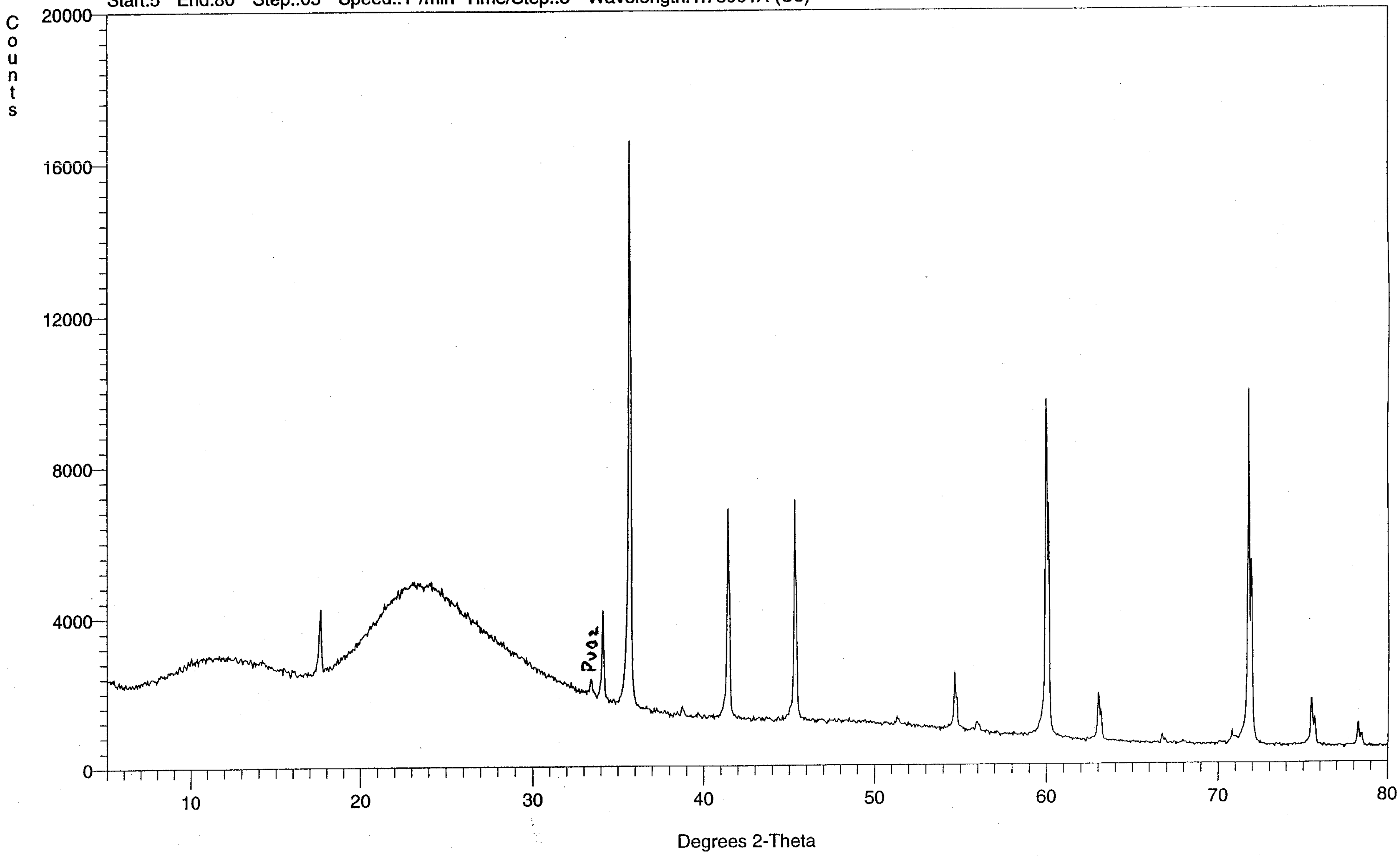
A.4 Pu-pyrochlore

The following Patterns have been sent as files. Print-outs of the data have been placed in this appendix.

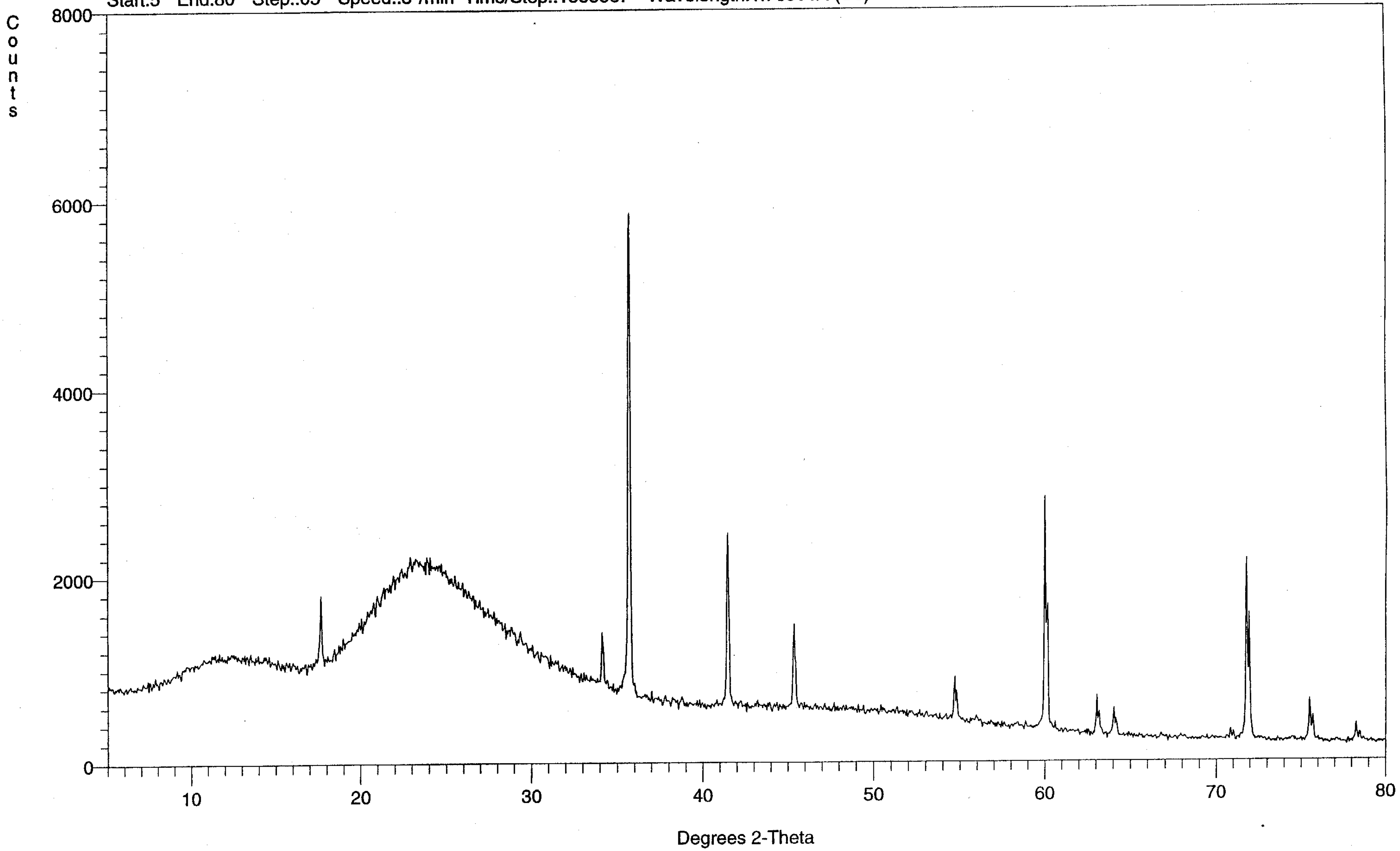
• Ground Surface Pu12403B (1490°C, 16 h., air)	s15847
• Ground Surface Pu12901B (1490°C, 16 h., air)	s15989

The broad peaks at ~ 12 and ~ 24 degrees 2 theta are due to the mounting resin.

File: e:\data\xrd\s15989.cpi Date: 11-18-1999 Comment: Pu-pyrochlore, 1490 deg. C, 16h., air, polished pellet (Pu12901B).
Start:5° End:80° Step:.05° Speed:.1°/min Time/Step:.5° Wavelength:1.78901Å (Co)



File: e:\data\xrd\s15847.cpi Date: 11-18-1999 Comment: Pu-pyrochlore 1490 deg. c, 16h., air, polished pellet. (Pu124-03B).
Start:5° End:80° Step:.05° Speed:.3°/min Time/Step:.1666667° Wavelength:1.78901Å (Co)



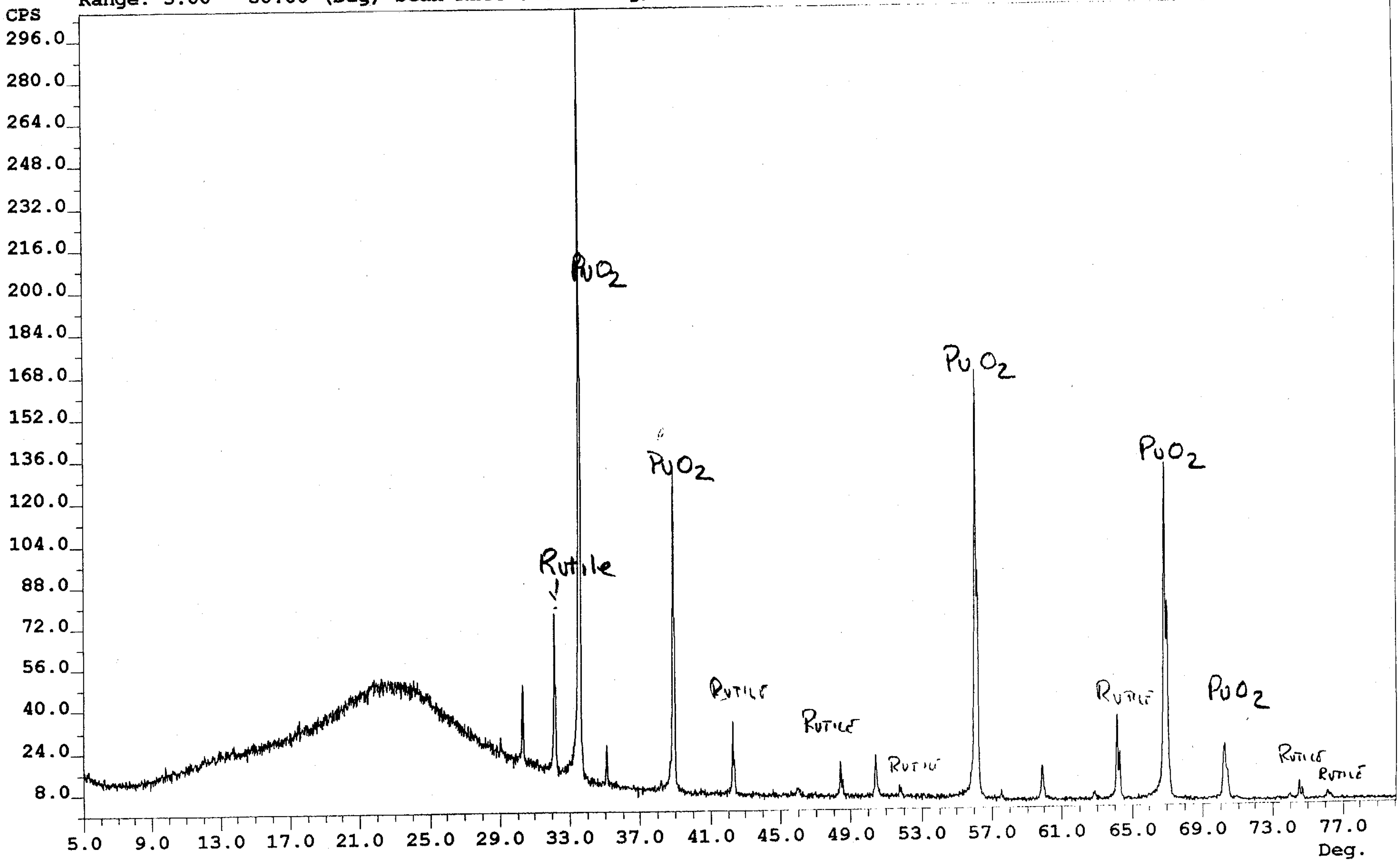
A.5 Pu-brannerite

The following Patterns have been sent as files. Print-outs of the data have been placed in this appendix.

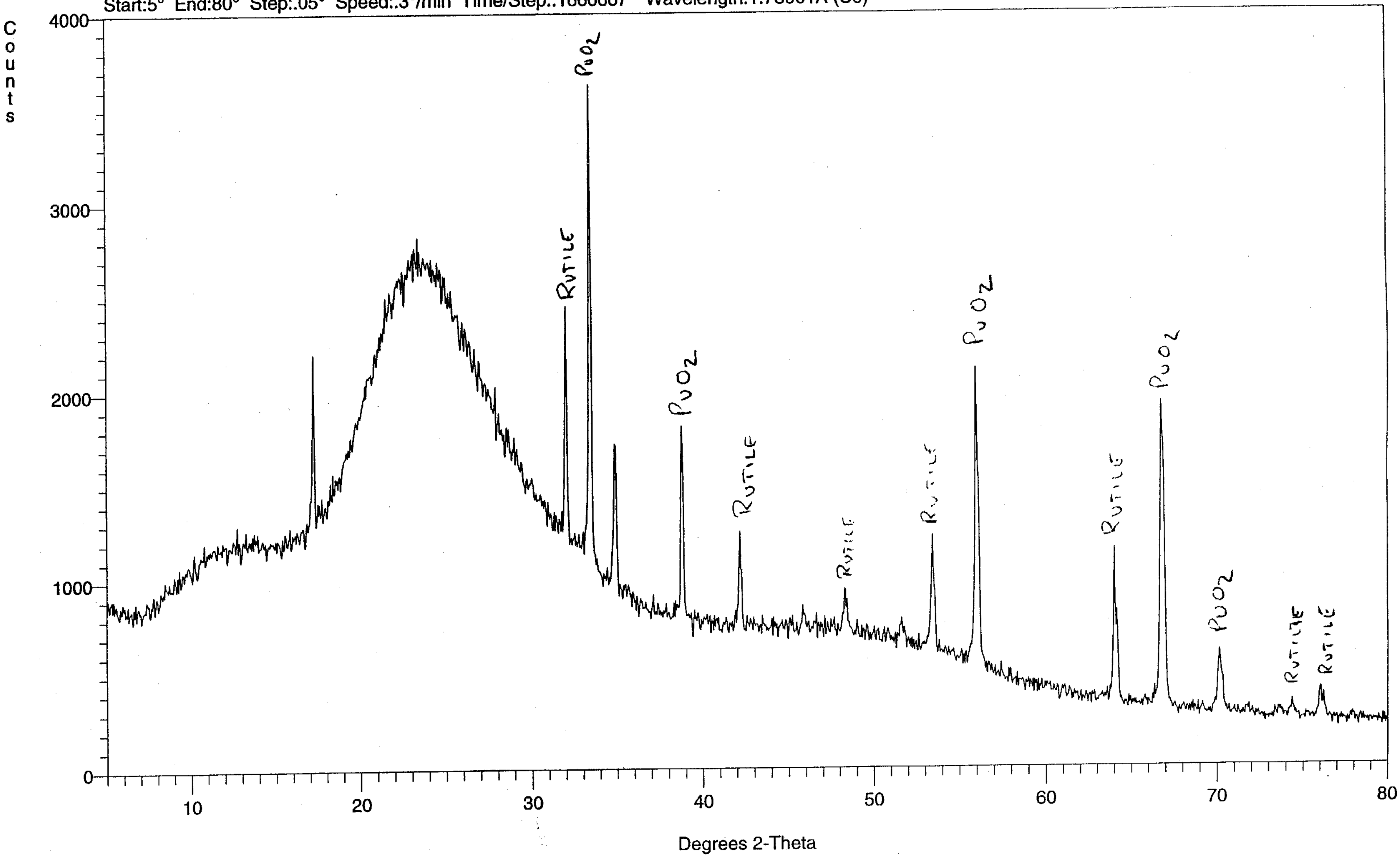
• Ground Surface Pu08202B (1550°C, 16 h., air)	t633
• Ground Surface Pu12502B (1525°C, 16 h., air)	s15692
• Ground Surface Pu12602B (1490°C, 16 h., air)	s15848

The broad peaks at ~ 12 and ~ 24 degrees 2 theta are due to the mounting resin.

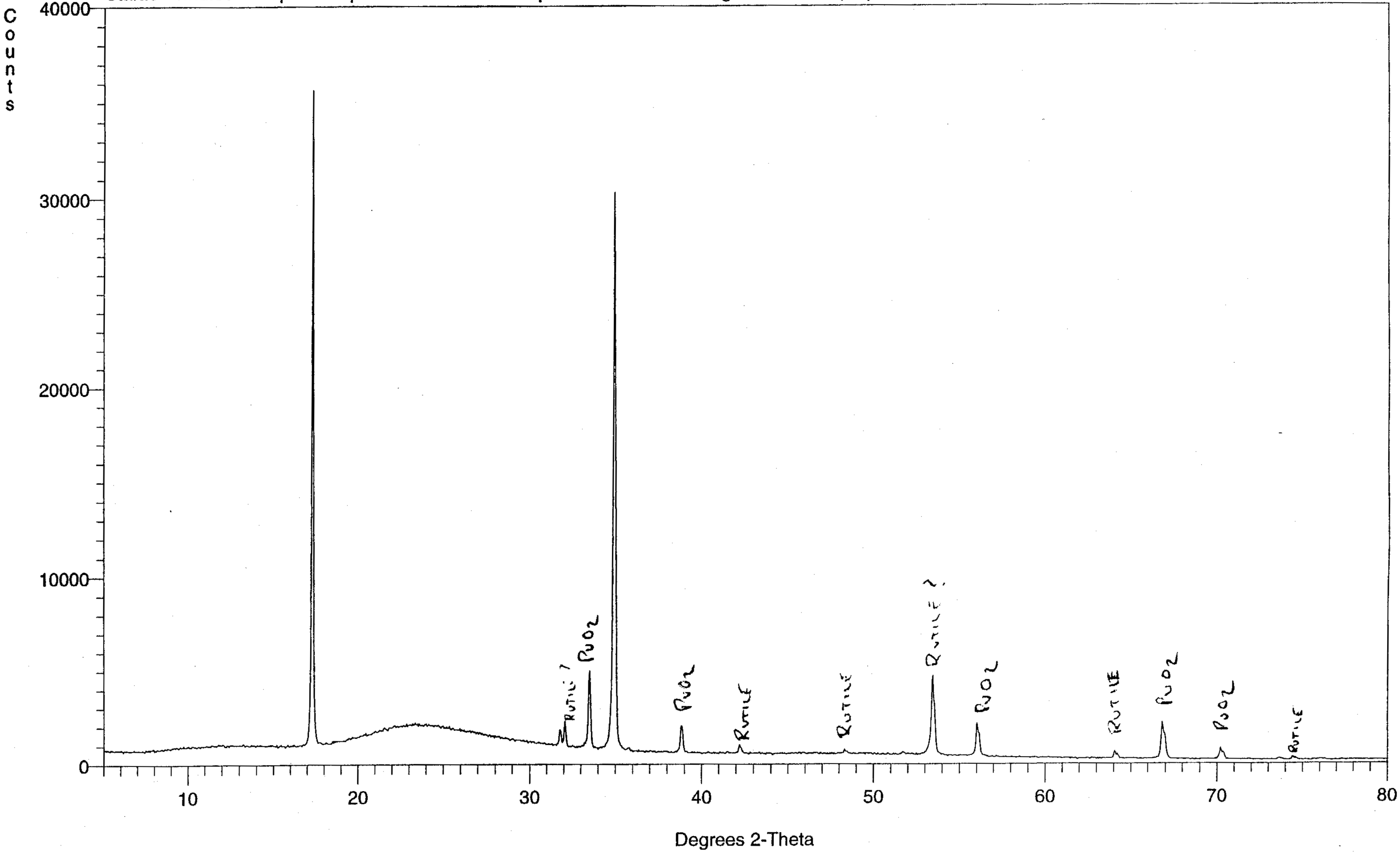
File: T633, ID: PU-82 PUTI206 1550°C, 16 hr, air Polished pellet.
Date: 09/07/98 11:49 Step : 0.020° Cnt Time: 15.000 Sec.
Range: 5.00 - 80.00 (Deg) Scan Rate : 0.00 Deg/min.



File: e:\data\xrd\s15692.cpi   Date: 11-18-1999   Comment: Pu-brannerite 1525 deg. C 16 h., air, polished pellet (Pu12502B).
Start:5° End:80° Step:.05° Speed:.3°/min Time/Step:.1666667° Wavelength:1.78901Å (Co)



File: e:\data\xrd\s15848.cpi Date: 11-18-1999 Comment: Pu-brannerite, 1490 deg. C, 16 h., air, polished pellet (Pu12602B)
Start:5° End:80° Step:.05° Speed:.3°/min Time/Step:.1666667° Wavelength:1.78901Å (Co)



A.6 4M Zirconolites

The following Patterns have been sent as files. Print-outs of the data have been placed in this appendix.

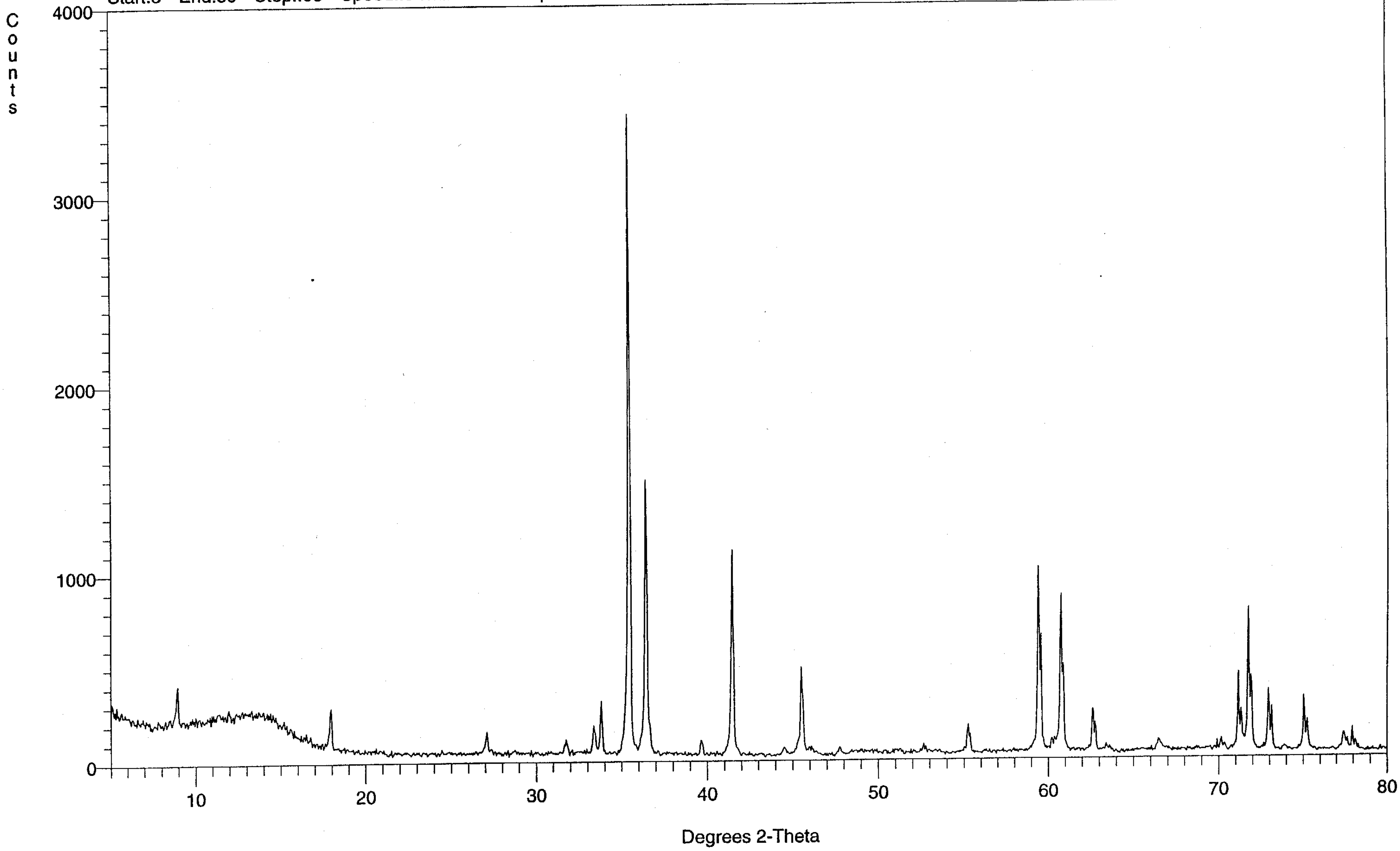
$Ca_{0.6}Gd_{0.8}Hf_{0.6}Ti_2O_7$ (mws980423 and mws99-0479) pellets sintered at 1500°C in air for 100 h and 50 h respectively.

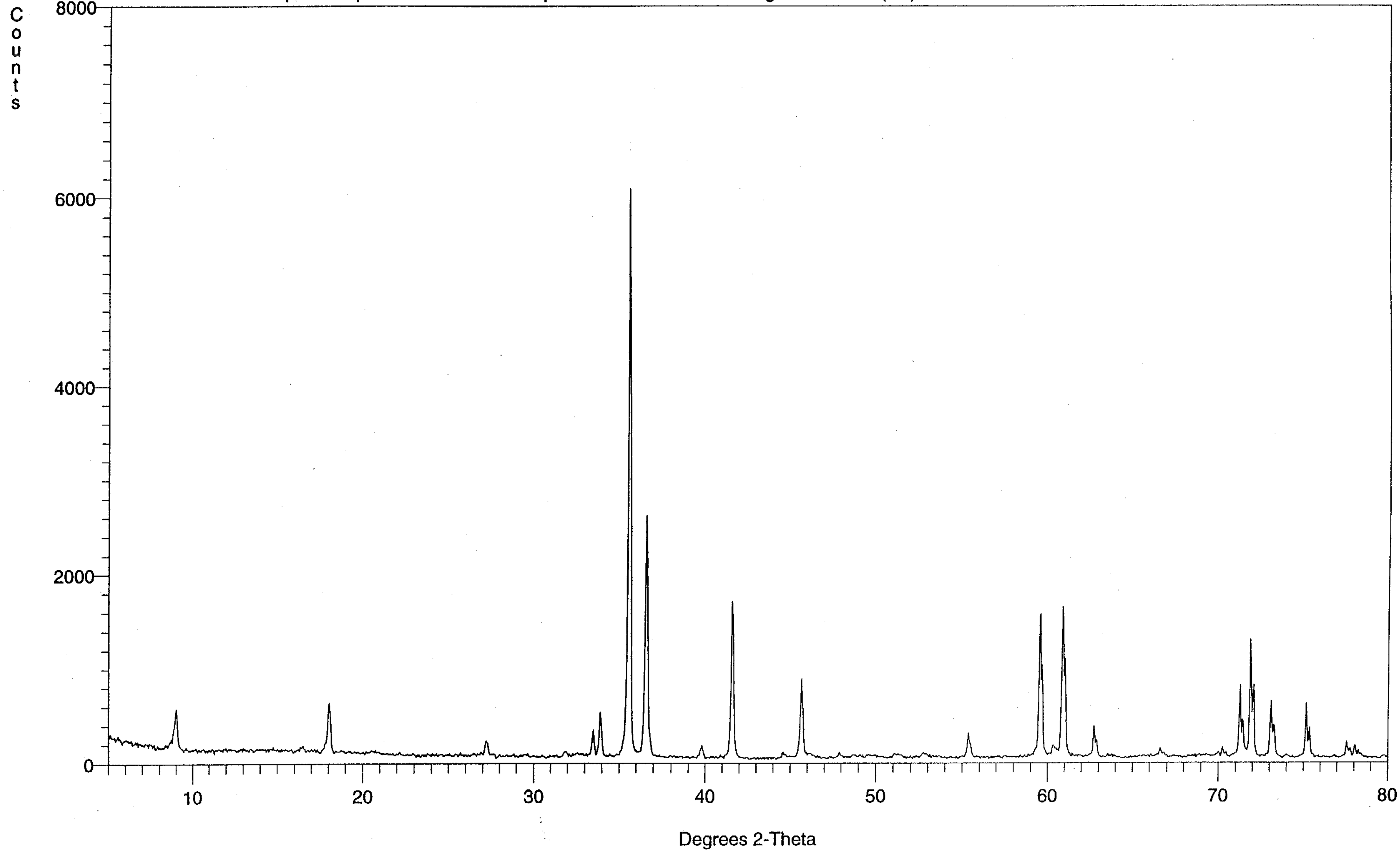
• Ground Surface	s15099
• Powder	s15965
• Powder with W	s15966

$Ca_{0.7}Gd_{0.6}Hf_{0.7}Ti_2O_7$ (mws980424 and mws99-0480) pellets sintered at 1500°C in air for 100 h and 50 h respectively.

• Ground Surface	s15101
• Powder	s15967
• Powder with W	s15968

File: e:\data\xrd\s15099.cpi   Date: 11-18-1999   Comment: 4M zirconolite ground pellet (mws980423).
Start:5° End:80° Step:.05° Speed:.3°/min Time/Step:.1666667° Wavelength:1.78901Å (Co)

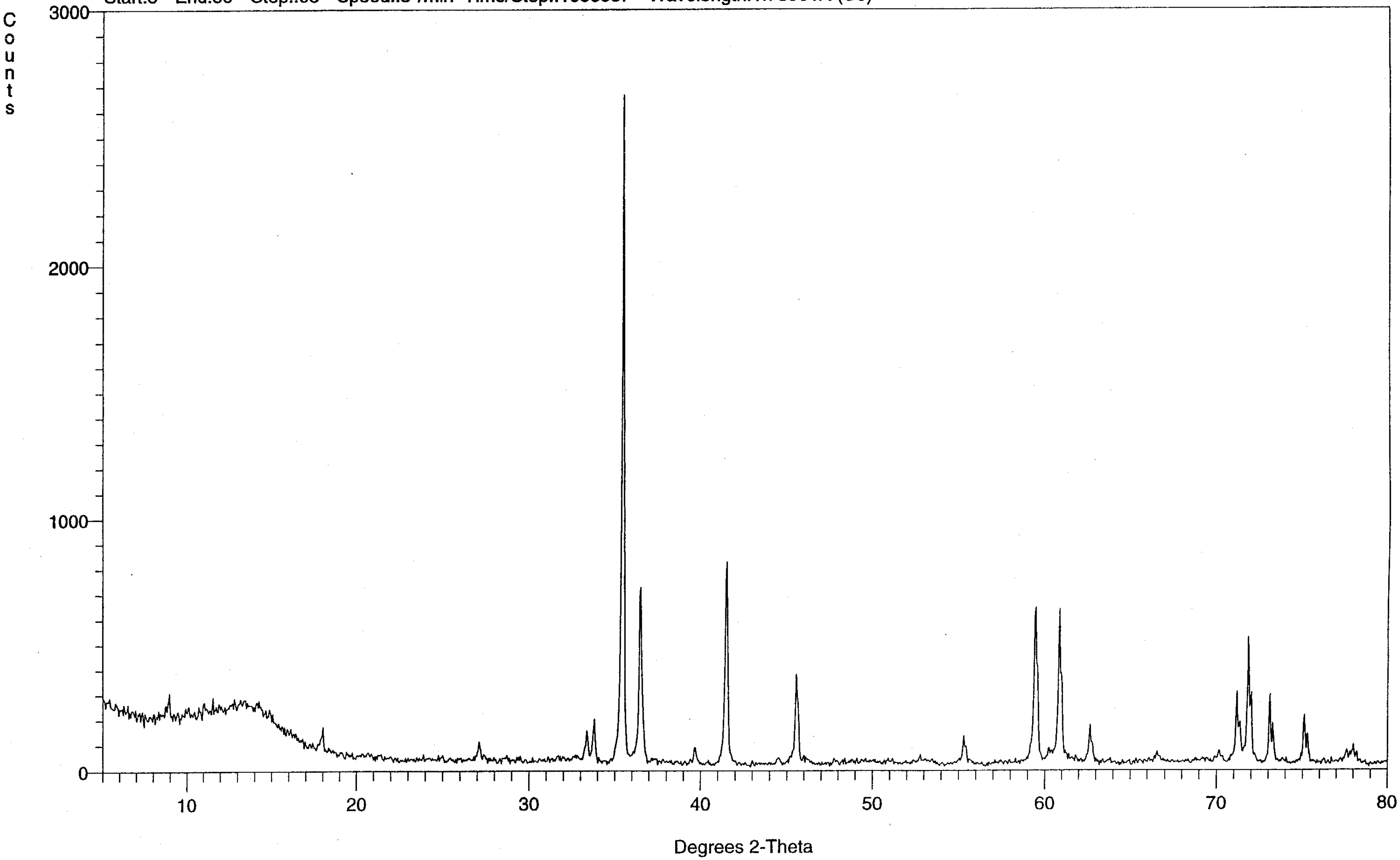




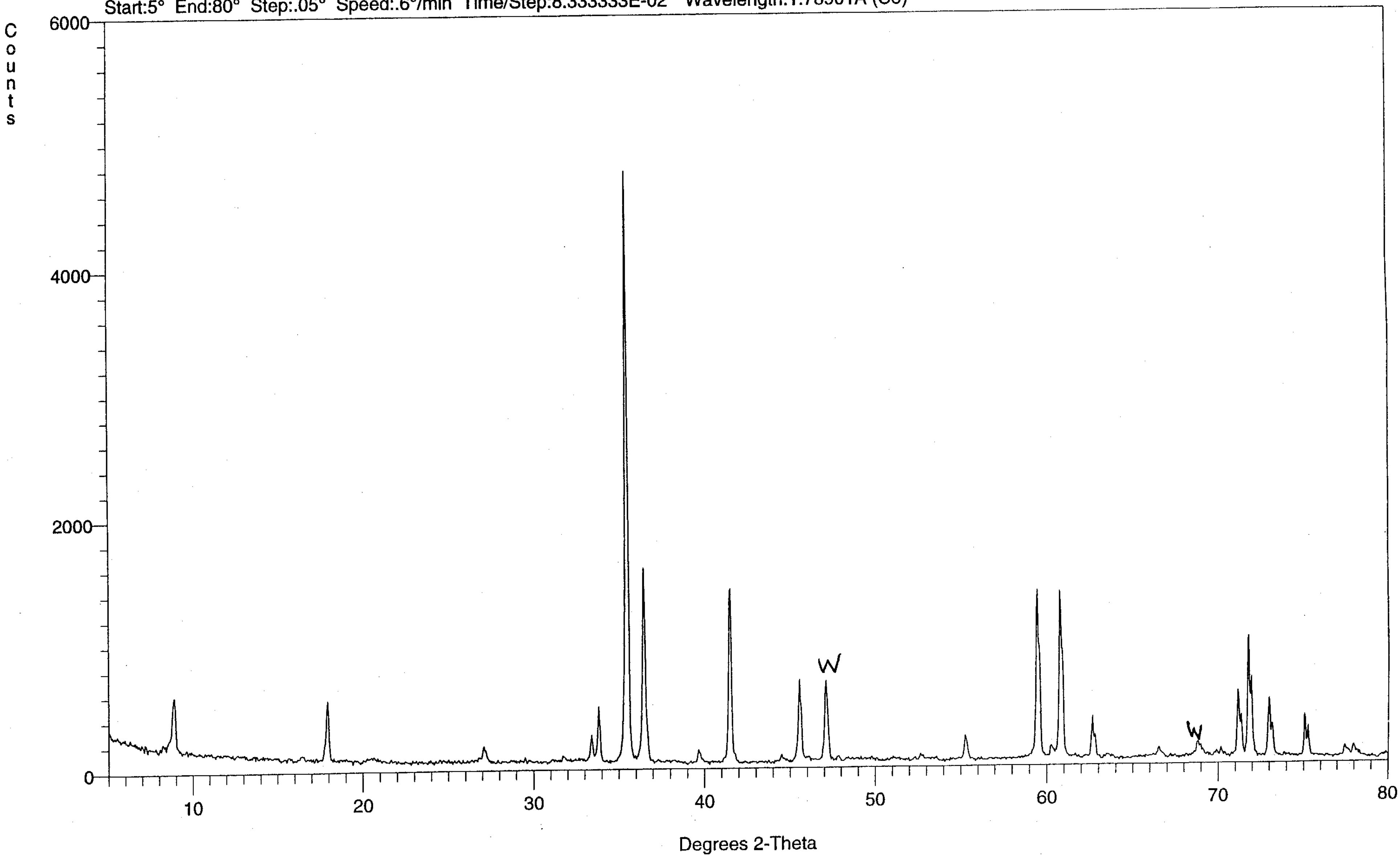
File: e:\data\xrd\s15965.cpi Date: 11-18-1999 Comment: 4M zirconolite powder (mws99-0479).
Start:5° End:80° Step:.05° Speed:.6°/min Time/Step:8.333333E-02° Wavelength:1.78901Å (Co)

File: e:\data\xrd\s15101.cpi   Date: 11-18-1999   Comment: 4M zirconolite ground pellet (mws980424)

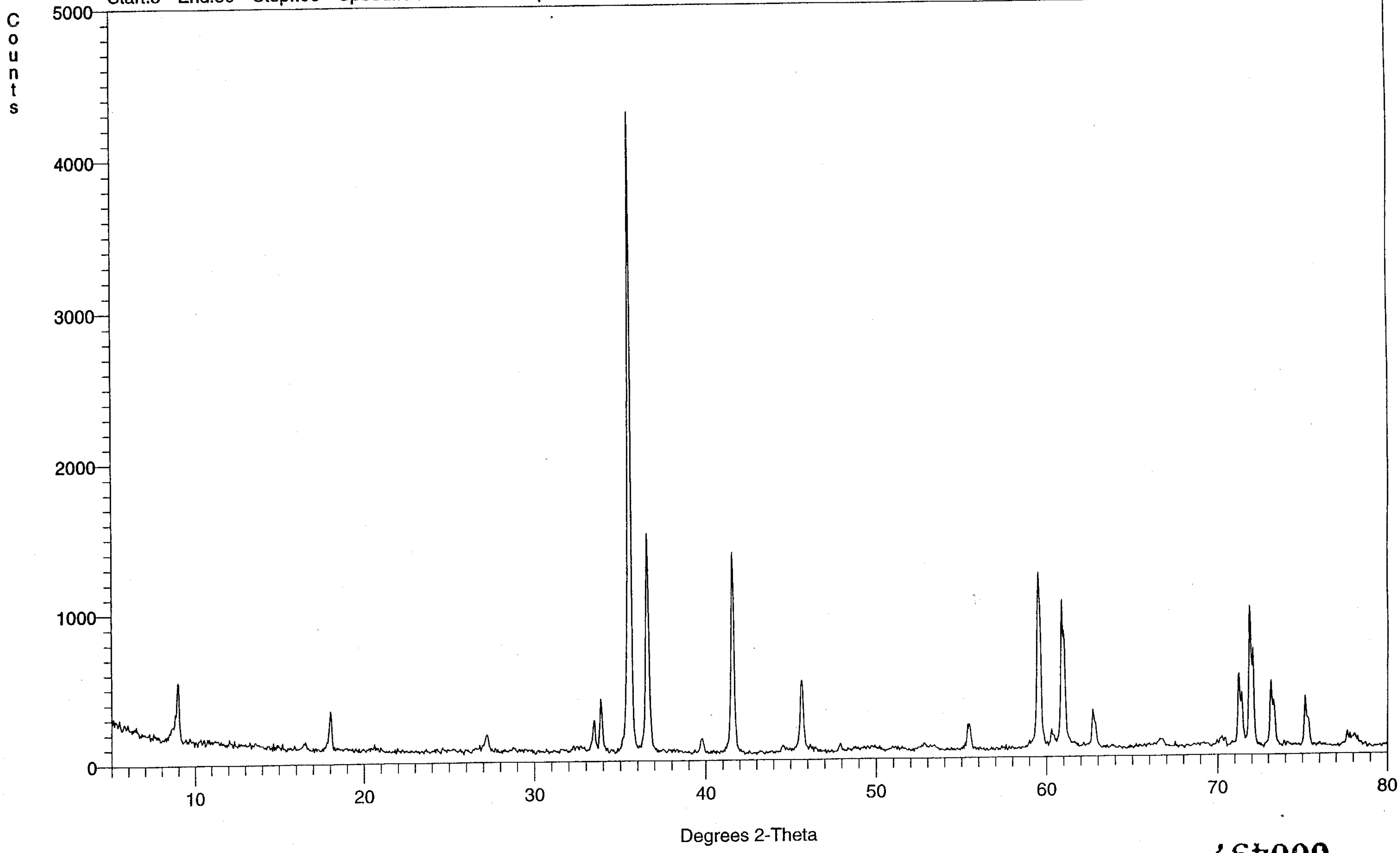
Start:5° End:80° Step:.05° Speed:.3°/min Time/Step:.1666667° Wavelength:1.78901Å (Co)



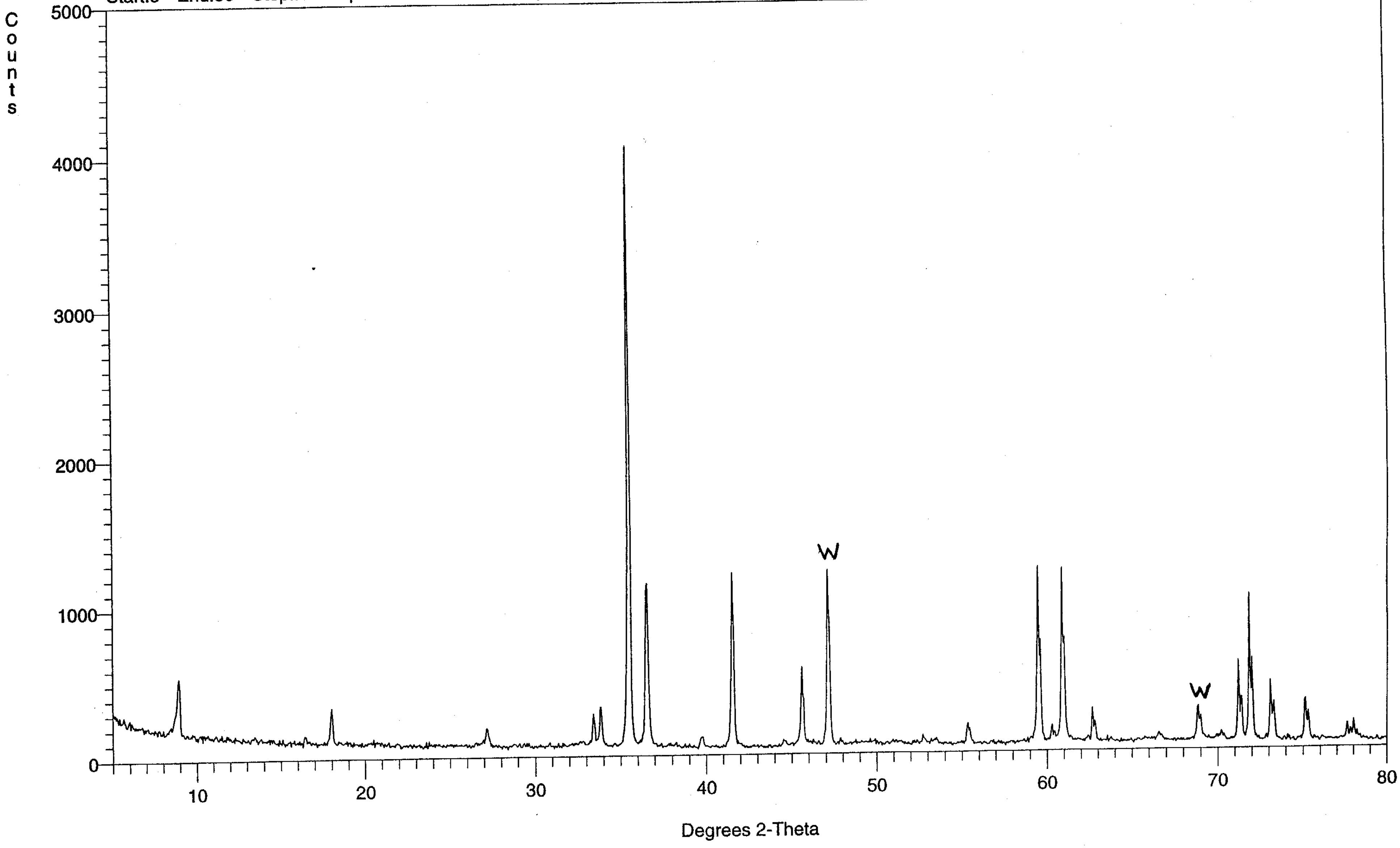
File: e:\data\xrd\s15966.cpi Date: 11-18-1999 Comment: 4M zirconolite powder with W (mws99-0479).
Start:5° End:80° Step:.05° Speed:.6°/min Time/Step:8.333333E-02° Wavelength:1.78901Å (Co)



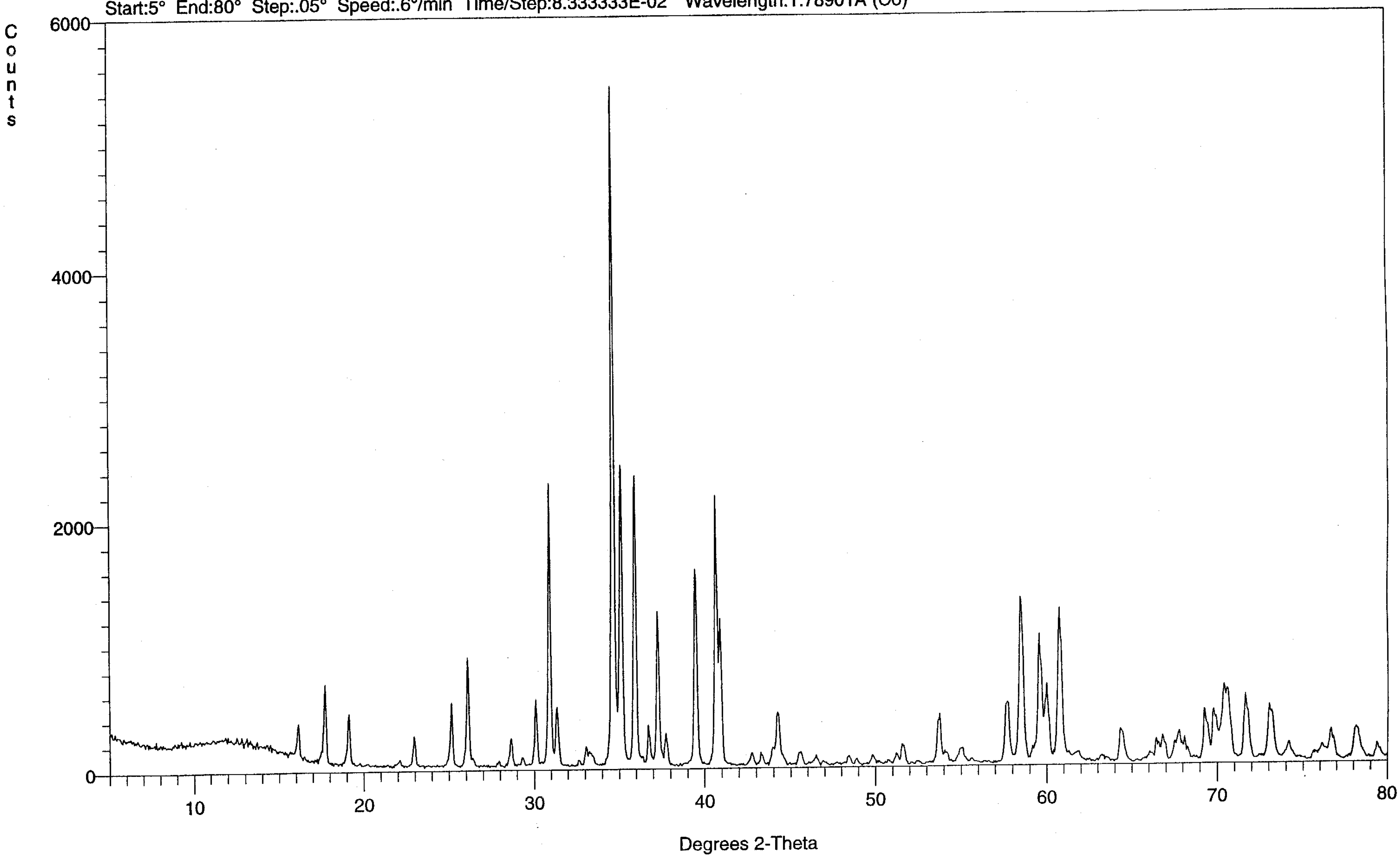
File: e:\data\xrd\s15967.cpi Date: 11-18-1999 Comment: 4M zirconolite powder (mws99-0480).
Start:5° End:80° Step:.05° Speed:.6°/min Time/Step:8.333333E-02° Wavelength:1.78901Å (Co)



File: e:\data\xrd\s15968.cpi Date: 11-18-1999 Comment: 4M zirconolite powder with W (mws99-0480).
Start:5° End:80° Step:.05° Speed:.6°/min Time/Step:8.333333E-02° Wavelength:1.78901Å (Co)



File: e:\data\xrd\s15820.cpi   Date: 11-18-1999   Comment: CaHfSn2O7 sintered 1600 deg. C 4 h., air ground pellet (mws99-0520).
Start:5° End:80° Step:.05° Speed:.6°/min Time/Step:8.333333E-02° Wavelength:1.78901Å (Co)



File: e:\data\xrd\s16011.cpi Date: 11-18-1999 Comment: CaHfSn2O7 sintered 1600 deg. C, 16 h air, ground pellet (mws99-0537)
Start:5° End:80° Step:.05° Speed:.3°/min Time/Step:.1666667° Wavelength:1.78901Å (Co)