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Cold Crucible Vitrification of Non-Radioactive CST and Simulated Hanford Tank Waste

August 2019

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Summary

The Direct Feed Low-Activity Waste (DFLAW) flowsheet provides for the initial production of immobilized low-activity waste (ILAW) by feeding low-activity waste (LAW) from tank farms to the Hanford Waste Treatment and Immobilization Plant (WTP) LAW Facility for immobilization. Prior to the transfer of feed to the WTP LAW Vitrification Facility, tank supernatant waste will be pretreated by the Tank-Side Cesium Removal (TSCR) system to meet the WTP LAW waste acceptance criteria ($<3.18\times 10^{-5}$ Ci ^{137}Cs/mole of Na). This pretreatment will remove cesium from the waste stream through ion exchange (IX). The selected media for IX is crystalline silicotitanate (CST).

The Cs is not easily removed from the CST; thus, the CST is described as non-elutable and will need to be managed with high ^{135}Cs and ^{137}Cs activity post processing. This report addresses the crucible vitrification of the cold (non-radioactive) CST medium into simulated high-level waste (HLW) glass to demonstrate vitrification of CST with other fractions of the waste during HLW operations and to develop a formulation of a CST-bearing melter feed.

Initially, three glass compositions were chosen based on fitting glass models to the CST composition and HLW composition to be used in the vitrification of the actual spent CST and actual Hanford tank waste while trying to maximize the CST loading in the glass. After preparation and initial analysis, these glasses were all heavily crystalline. Therefore, it was decided to not proceed with testing of these glasses and instead design a glass with a lower waste loading of 10% CST and 33% HLW sludge simulant and 57% glass forming chemicals that would melt well and not form crystals during heat treating. Glass CST19-04 was the only glass that, after melting twice at 1150°C, being treated with the CCC slow cool curve, and heat treating at 950°C for 24 h, formed no crystals. Therefore, it was decided to proceed with testing of this glass and not the others. This glass was melted and fully characterized by canister centerline cooling (CCC), crystal fraction, Product Consistency Test (PCT), Toxicity Characteristic Leaching Procedure (TCLP), viscosity, and electrical conductivity as shown in Table S.1. These results show that this glass met all required constraints for the HLW glass.

This testing showed that CST can successfully be added to HLW glass and produce a glass that meets all durability and processing constraints. Overall, the first three glasses tested showed that the design was above the maximum loading of the CST in a glass of this formulation and was not able to produce glass. The fourth glass with lower waste loading was successfully incorporated into glass. However, based on tank waste composition, the waste loading of the glass may need to be varied to produce a successful glass.

Table S.1. CST19-04 Glass Characteristics

Characteristic	Result
CCC	Amorphous
Crystal Fraction at 950°C	Amorphous
Viscosity	2.63 Pa-s
Electrical Conductivity	35.5 S/m
PCT of quenched glass (Normalized Mass Loss)	B = 1.28 g/m^2 Li = 1.14 g/m^2 Na = 0.65 g/m^2 Si = 0.15 g/m^2
PCT of CCC glass (Normalized Mass Loss)	B = 1.22 g/m^2 Li = 1.11 g/m^2 Na = 0.62 g/m^2 Si = 0.17 g/m^2
TCLP of quenched glass	Ag = 0.0144 mg/L (spike didn't meet criteria) As = <0.025 mg/L Ba = <0.005 mg/L Cd = <0.005 mg/L Cr = <0.005 mg/L Pb = 0.012 mg/L Hg = <0.0001 mg/L Se = <0.025 mg/L
TCLP of CCC glass	Ag = 0.0356 mg/L (spike didn't meet criteria) As = <0.025 mg/L Ba = <0.005 mg/L Cd = <0.005 mg/L Cr = <0.005 mg/L Pb = 0.0202 mg/L Hg = <0.0001 mg/L Se = <0.025 mg/L

Acknowledgments

The authors would like to thank Tatiana Levitskaia for her help, Derek Dixon for reviewing the glass calculation files, test data packages, and this technical report, Bill Dey for reviews to ensure compliance with strict quality assurance standards, and Matt Wilburn for technical editing of this report.

Acronyms and Abbreviations

CCC	canister centerline cooling
CF	crystal fraction
CST	crystalline silicotitanate
DFLAW	Direct Feed Low-Activity Waste
DWPF	Defense Waste Processing Facility
EC	electrical conductivity
EPA	U.S. Environmental Protection Agency
GFC	glass-forming chemical
HLW	high-level waste
ICP-AES	inductively coupled plasma–atomic emission spectroscopy
ILAW	immobilized low-activity waste
IX	ion exchange
LAW	low-activity waste
NR	normalized release
PCT	Product Consistency Test
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
RCRA	Resource Conservation and Recovery Act
SwRI	Southwest Research Institute
TCLP	Toxicity Characteristic Leaching Procedure
TSCR	Tank-Side Cesium Removal
UTS	Universal Treatment Standards
WRPS	Washington River Protection Solutions
WTP	Hanford Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program
XRD	X-ray diffraction

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1.0 Introduction

The Direct Feed Low-Activity Waste (DFLAW) flowsheet provides for the initial production of immobilized low-activity waste (ILAW) by feeding low-activity waste (LAW) from Hanford tank farms to the Hanford Waste Treatment and Immobilization Plant (WTP). Prior to the transfer of feed to the WTP LAW Vitrification Facility, tank waste supernatant will be pretreated by the Tank-Side Cesium Removal (TSCR) system to meet the WTP LAW waste acceptance criteria ($<3.18\times10^{-5}$ Ci ^{137}Cs/mole of Na). This pretreatment will remove cesium from the waste stream through ion exchange (IX). The selected media for IX is crystalline silicotitanate (CST), manufactured in a granular, nominally spherical (engineered) form by Honeywell UOP LLC (Des Plaines, IL).

The Cs is not easily removed from the CST; thus, the CST is described as non-elutable and will need to be managed with high ^{135}Cs and ^{137}Cs activity post processing. Testing was requested by Washington River Protection Solutions (WRPS) to demonstrate vitrification of CST with other fractions of the waste during high-level waste (HLW) operations. This report addresses the crucible vitrification of the cold (non-radioactive) CST medium into simulated HLW glass to demonstrate vitrification of CST with other fractions of the waste during HLW operations and to develop a formulation of a CST-bearing melter feed that meets plant standards. Once a formulation of a CST-bearing melter feed is determined, it will be applied to the vitrification of actual spent CST used for processing of actual filtered Hanford tank waste supernatants. The results of the vitrification of actual spent CST will be presented in a separate report.

Four target glass compositions for immobilization of CST to achieve target glass properties were identified through modeling of the formulation using existing glass property models developed at Pacific Northwest National Laboratory (PNNL) by Vienna et al. (2016) trying to maximize the CST loading in the glass. The existing PNNL models do not include elemental constituents of the CST. Therefore, they were augmented with the CST vitrification results available in the literature reports as well as CST loading characterization data (Fox and Edwards 2010; Kot et al. 2017; Matlack et al. 2018). The glass formulation parameters include variable loadings of the sludge simulant, glass-forming chemicals (GFCs), and CST to identify formulations that minimize crystallinity in the molten glass upon slow cooling while simultaneously satisfying other glass property constraints. Based on these results, a candidate glass formulation was selected for the crucible fabrication and characterization. This candidate glass formulation was prepared and was composed of simulated CST IX media and HLW sludge along with added GFCs.

Recent work at Savannah River National Laboratory (Fox and Edwards 2010), while helpful to this work, did not contain waste compositions that were representative of Hanford HLW sludge chemistry. For instance, Hanford HLW sludge chemistries contain higher Cr and Al, both of which can lead to crystallization, e.g., Cr strongly increases spinel crystallization and Al increases both spinel and nepheline crystallization. While spinel can settle in the melter, causing melter processing issues, and settle in the glass pour spout, interfering with glass pouring, the process of nepheline crystallization results in a residual glass that is less chemically durable once Al is removed from the glass network. Thus, to evaluate the crystallization behavior in the simulated CST-containing HLW glasses upon quenching, heat treatment at different temperatures, slow cooling, and after a canister centerline cooling (CCC) profile was performed, the crystal fraction (CF) was determined by X-ray diffraction (XRD). To assess the effects of composition on the chemical durabilities of selected glass products, the Product Consistency Test (PCT) and Toxicity Characteristic Leaching Procedure (TCLP) were performed on the most promising glass. Additional physical properties of viscosity and electrical conductivity (EC) were also evaluated for the most promising composition. These results are all reported here.

1.1 Quality Assurance

All research and development (R&D) work at PNNL is performed in accordance with PNNL's Laboratory-Level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications* (ASME 2000), to R&D activities. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the PNNL's WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for this work. The WWFTP QA program implements the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications* (ASME 2008), and NQA-1a-2009, *Addenda to ASME NQA-1-2008* (ASME 2009). These are implemented through the *WWFTP Quality Assurance Plan* (QA-WWFTP-001) and associated QA-NSLW-numbered procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work.

The work described in this report was assigned the technology level "Applied Research" and was planned, performed, documented, and reported in accordance with procedure QA-NSLW-1102, *Scientific Investigation for Applied Research*. All staff members contributing to the work received proper technical and QA training prior to performing quality-affecting work

2.0 Test Methods

This section describes how the data was obtained for these glasses, including the glass fabrication, chemical composition analysis, centerline cooling, CF, secondary phase identification, viscosity, EC, PCT, and TCLP measurements for the test glasses.

2.1 Glass Fabrication

The initial glass fabrication was performed according to the PNNL procedure *Glass Batching and Melting* (WFDL-GBM-1, Rev 2).[1] Single metal oxides, single metal carbonates, and sodium salts were mixed in the appropriate masses to form the target composition of the three initial glasses (see chemical compositions and component mass fractions below in Table 2.1) and placed in a plastic bag. After thoroughly mixing in the plastic bag for at least 30 s until a uniform color was observed, the powders were transferred into an agate milling chamber and milled for 2 min in the Angstrom vibratory mill. The powders were then transferred to a clean Pt-10%Rh crucible for melting using a two-step melt process. The first melt was of raw materials, performed at 1150°C for 1 h for the compositions to melt and form macroscopically homogenous glasses. To prepare the glasses for a second melt, the quenched glass from the first melt was ground to a fine powder in a tungsten carbide vibratory mill. The second melt was at the same temperature as the initial melt and 1 h in duration. However, the CST19-01 glass did not form an amorphous glass after this second melt (Figure 2.1), so it was melted a third time at 1200°C for 1 h. An amorphous glass still did not form, so a fourth melt was performed at 1250°C for 2 h. After this melt, an amorphous glass was formed (Figure 2.1). See Appendix A for photos of each of the glasses after melting and cooling.

Table 2.1. Targeted Compositions (Mass Fractions) for the Initial CST Glass Compositions

	Glass ID		
Component	CST19-01	CST19-02	CST19-03
Ag_2O	0.0012	0.0012	0.0013
Al_2O_3	0.1366	0.1469	0.1514
B_2O_3	0.0686	0.0981	0.1299
CaO	0.0014	0.0014	0.0015
CeO_2	0.0005	0.0006	0.0006
Cs_2O	0.0008	0.0005	0.0003
F	0.0010	0.0011	0.0011
Fe_2O_3	0.0266	0.0286	0.0295
Li_2O	0.0091	0.0121	0.0114
MnO	0.0026	0.0028	0.0029
Na_2O	0.2140	0.2141	0.2140
Nb_2O_5	0.0493	0.0344	0.0229
Nd_2O_3	0.0613	0.0659	0.0680
NiO	0.0006	0.0006	0.0007

[1] Russell RL. 2016. *Glass Batching and Melting.* WFDL-GBM-1, Rev. 2. This document is internal to PNNL and is not publicly available.

	Glass ID		
Component	CST19-01	CST19-02	CST19-03
P_2O_5	0.0027	0.0029	0.0029
PbO	0.0005	0.0005	0.0005
SiO_2	0.3030	0.3031	0.3030
TiO_2	0.0787	0.0549	0.0366
ZrO_2	0.0414	0.0302	0.0215
Total	**0.9999**	**0.9999**	**1.0000**
Waste Loading			
Loaded CST	0.2150	0.1500	0.1000
HLW Sludge	0.3640	0.3920	0.4040
SiO_2	0.2440	0.2550	0.2630
H_3BO_3	0.0690	0.0980	0.1300
Li_2CO_3	0.0090	0.0120	0.0110
Na_2CO_3	0.0990	0.0930	0.0910
Total	**1.0000**	**1.0000**	**0.9990**

Figure 2.1. Glass CST19-01 after melting at 1150°C for 1 hour (left) and at 1250°C for 2 hours (right).

Two of the candidate glasses (CST19-02 and CST19-03) were also fabricated by starting with a simulated HLW sludge based on Tank 241-C-104 waste composition (Cantrell et al. 2015) (see Table 2.2) and adding pre-treated CST IX media (see Table 2.3) along with the GFCs (see Table 2.4), both as described below.

Table 2.2. Composition of the HLW Sludge Simulant (Mass Fraction)

Component	Mass Fraction
Ag_2O	0.0026
Al_2O_3	0.4663
CaO	0.0030

Component	Mass Fraction
CdO	0.0003
Ce_2O_3	0.0011
Cr_2O_3	0.0020
F	0.0021
Fe_2O_3	0.0642
MnO	0.0056
Na_2O	0.2595
Nd_2O_3	0.1282
NiO	0.0015
P_2O_5	0.0067
PbO	0.0013
SiO_2	0.0480
ZrO_2	0.0077
Total	**1.0001**

The CST IX media (Lot# 2002009604) was pretreated by washing in 0.1M NaOH and then decanting. Nominally, one volume CST was contacted with three volumes 0.1M NaOH. This was repeated three times, at which point the contacted 0.1M NaOH solution was still not completely clear, as shown in Figure 2.2, indicating that some fines were still present in the CST but not a concern. Therefore, this wash solution was decanted, and the CST IX media was dried to a free-flowing form.

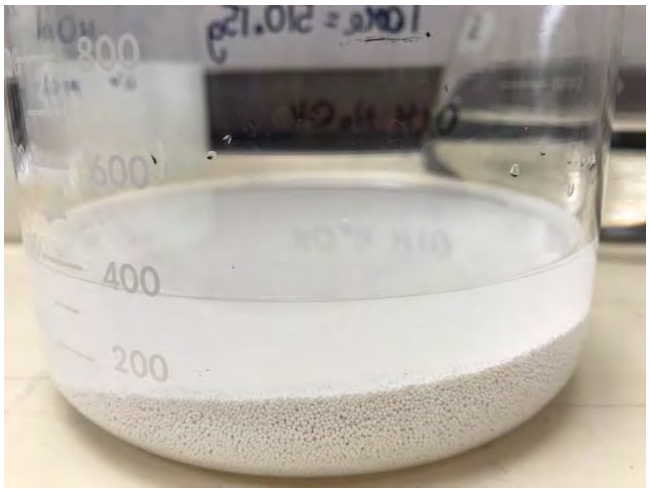

Figure 2.2. CST IX media after washing three times in 0.1M NaOH.

The CST loading solution was prepared in a 1-L volumetric flask by adding the chemicals listed in Table 2.2 one at a time in the order given. This composition was chosen based on the cations that primarily load onto CST in the approximate ratios of tank supernate. After each chemical addition, the solution was mixed until the chemical was dissolved. Once all the chemicals had been added and dissolved, the volume was adjusted with deionized water. Two separate batches were prepared.

Table 2.3. Composition of the CST Loading Solution

Component	Target Amount (g)
$NaNO_3$	170.00
$CsNO_3$	0.0156
$CaCl_2$	0.1100
KCl	0.1100
50% NaOH solution	56.00

Batches weighing 125 g of the free-flowing pretreated CST IX media were aliquoted into separate 2-L polyethylene bottles for each loading sample. The CST mass aliquot was targeted to achieve a phase ratio (volume of liquid to mass of dry CST) of 200. The CST was contacted with 1 L of the CST loading solution. The loading bottles were placed upright in an orbital shaker with a 4-mm shaker diameter set to ~700 revolutions per minute. Rigorous mixing was observed for all samples; however, the CST remained on the floor of the bottle. This was not considered a problem because the solution was mixing well for contact with the CST. The CST was contacted with the solution for 72 h. The temperature was not controlled. After contact, the bottles were shaken and the CST was allowed to settle, after which the aqueous fraction was removed, and the CST was dried again to a free-flowing form.

The simulated HLW sludge was prepared by adding the chemicals listed in Table 2.2 into a 5-L bucket and stirred until a uniform mixture was obtained. Once a uniform mixture was obtained, it was heated while mixing until it was too thick to mix. The mixer was then removed, and the sludge was transferred to a 105°C oven where it continued to be dried. Once completely dry, the clumps were broken up and the sludge was mixed in a tungsten carbide milling chamber until powdered.

The simulated CST glasses were then prepared by mixing the glass components in the appropriate masses to form the two target glass compositions (see Table 2.4). Each glass was melted in a Pt-alloy crucible using a two-step melt process. The first melt was of the glass components that had been mechanically mixed in an agate milling chamber for 2 min. Melting was performed at 1150°C for 1 h for the compositions to melt and form macroscopically homogenous glasses. A second melt of the glass was accomplished after the quenched glass from the first melt was ground to a fine powder in a tungsten carbide vibratory mill. The second melt was at the same temperature as the initial melt and 1 h in duration.

Table 2.4. Targeted Compositions (Mass Fractions) for the CST Glass Compositions

	Glass ID	
Component	CST19-CST-02	CST19-CST-03
Loaded CST	0.150	0.100
HLW Sludge	0.392	0.404
SiO_2	0.255	0.263
H_3BO_3	0.098	0.130
Li_2CO_3	0.012	0.011
Na_2CO_3	0.093	0.091
Total	**1.000**	**0.999**

After these melts, it was determined that these glasses produced considerable amounts of nepheline during the CCC testing, indicating that they would probably not pass the standards required of HLW glass. Nepheline (nominally $NaAlSiO_4$) is a major concern because it can reduce the durability of the resulting glass by removing three moles of glass former oxides (one mole of Al_2O_3 and two moles of SiO_2) for every mole of Na_2O. Therefore, a fourth glass composition with reduced waste loading mass fractions was prepared from the oxide chemicals using the same method as the first three compositions described above. This composition is shown in Table 2.5 based on a mass fraction of 0.10 CST and 0.33 HLW sludge and 0.57 glass formers along with each chemical mass fraction used.

Table 2.5. Targeted Compositions (Mass Fractions) for the Fourth CST Glass Composition

	Glass ID
Component	CST19-04
Ag_2O	0.0011
Al_2O_3	0.1251
B_2O_3	0.1803
CaO	0.0012
CeO_2	0.0005
Cs_2O	0.0003
F	0.0009
Fe_2O_3	0.0244
Li_2O	0.0391
MnO	0.0024
Na_2O	0.1066
Nb_2O_5	0.0229
Nd_2O_3	0.0562
NiO	0.0005
P_2O_5	0.0024
PbO	0.0004
SiO_2	0.3781
TiO_2	0.0366
ZrO_2	0.0208
Total	**0.9998**
Waste Loading	
Loaded CST	0.1000
HLW Sludge	0.3300
SiO_2	0.3420
H_3BO_3	0.1800
Li_2CO_3	0.0390
Na_2CO_3	0.0050
Total	**1.0000**

2.2 Chemical Analysis of Glass Composition

To confirm that the "as-fabricated" CST19-04 glass corresponded to the specified target composition, a representative sample of the glass was chemically analyzed at the Southwest Research Institute (SwRI) by inductively coupled plasma–atomic emission spectroscopy (ICP-AES). These results are discussed in Section 3.1.

2.3 Canister Centerline Cooling and Crystal Identification

A portion (~100 g) of each test glass was subjected to a simulated CCC heat treatment according to the simulated CCC temperature profile shown in Table 2.6 and Figure 2.3. This profile is the temperature schedule of CCC treatment for Hanford HLW glasses planned for use at WTP.[1] Pieces of quenched glass <3 cm in diameter were placed in a Pt-alloy crucible and covered with a Pt-alloy lid. The glass samples in simulated CCC treatment were brought to a target temperature of the glass melting temperature and held for 30 min. Then they were quickly cooled to 1050°C. The cooling profile was then started at 1050°C and progressed down to about 400°C based on seven cooling segments shown in Table 2.6. The starting temperature for the seven segments of cooling are 1050°C, 980°C, 930°C, 875°C, 825°C, 775°C, and 725°C.

Table 2.6. Canister Center Line Cooling Profile for Hanford HLW Glass

Canister Centerline Cooling Treatment Schedule		
Segment	Start-Stop Temp. (°C)	Rate (°C/min)
1	1050–980	–1.556
2	980–930	–0.807
3	930–875	–0.591
4	875–825	–0.388
5	825–775	–0.253
6	775–725	–0.278
7	725–400	–0.303

[1] Petkus LL. 2003. "Canister Centerline Cooling Data, Revision 1," to CA Musick, CCN: 074851, October 29, 2003, River Protection Project, Hanford Waste Treatment and Immobilization Plant, Richland, Washington. This document is not publicly available.

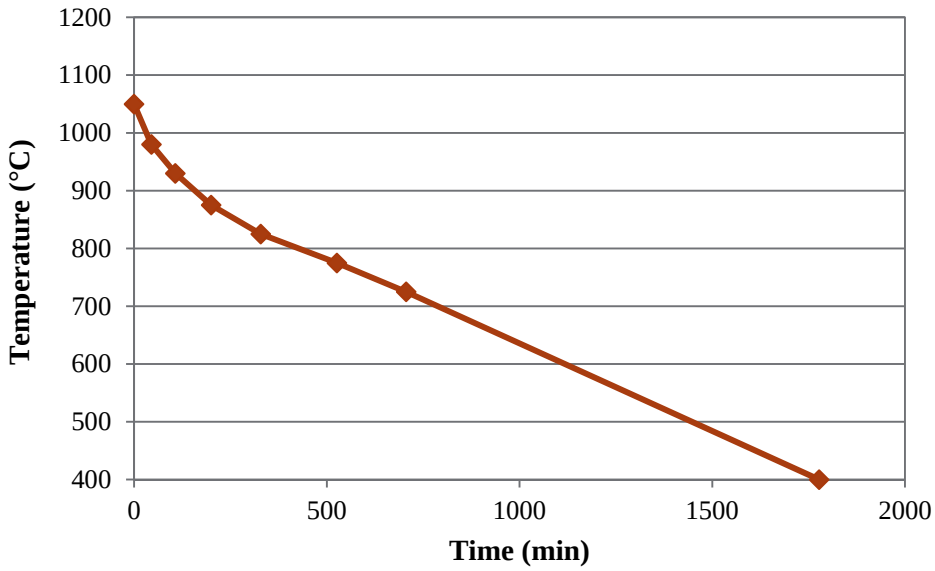

Figure 2.3. Plot of temperature schedule during CCC treatment of Hanford HLW glasses.

The amount and type of crystalline phases that formed during CCC treatment were analyzed by X-ray diffraction (XRD) according to Section 12.4.4 of the standard ASTM International procedure *Standard Test Method for Determining Liquidus Temperature of Waste Glasses and Simulated Waste Glasses* (ASTM C1720). Powdered glass samples were prepared using roughly 5 wt% ZnO as an internal standard phase with between 1.0 and 1.5 g of powdered glass. Glass and ZnO were milled together for 2 min in a 10-cm^3 tungsten carbide disc mill. The powdered glass samples were loaded into XRD sample holders and scanned using a Bruker D8 Advance XRD (Bruker AXS Inc., Madison, Wisconsin) with Cu Kα emission at a 0.04° 2θ step size, 4-s dwell time, from 10° to 70° 2θ scan range. XRD spectra were analyzed with TOPAS® 4.2 Software (Bruker AXS Inc., Madison, Wisconsin) for phase identification and Rietveld refinement to semi-quantify the amounts of crystal phases on some samples with high crystalline content. These results are discussed in Section 3.2.

2.4 Equilibrium Crystal Fraction

Equilibrium CF as a function of temperature (C_T) was measured in Pt-alloy crucibles and boats with tight-fitting lids (to minimize volatility) according to the standard ASTM International procedure *Standard Test Method for Determining Liquidus Temperature of Waste Glasses and Simulated Waste Glasses* (ASTM C1720). The heat treatment times and temperatures were 24 ±2 h at 850°C to 1150°C to ensure equilibrium was achieved without excessive volatility. The samples were then quenched and analyzed by XRD.

The C_Ts of each crystalline phase formed during heat treatment was analyzed by XRD according to Section 12.4.4 of ASTM C1720. Powdered glass samples were prepared using roughly 5 wt% ZnO as an internal standard phase with between 1.0 and 1.5 g of glass powder. Glass and ZnO were milled together for 2 min in a 10-cm^3 tungsten carbide disc mill. The powdered samples were loaded into plastic holders and analyzed using a Bruker D8 Advance XRD (Bruker AXS Inc., Madison, Wisconsin) with Cu Kα emission. Samples were scanned at a 0.04° 2θ step size, 4-s dwell time, from 10° to 70° 2θ scan range. XRD spectra were analyzed with TOPAS® 4.2 Software (Bruker AXS Inc., Madison, Wisconsin) for phase identification. Full-pattern Rietveld refinement using EVA® Software (Bruker AXS Inc., Madison,

Wisconsin) was performed to quantify the amounts of crystal phases on some samples with high crystalline content. These results are discussed in Section 3.3.

2.5 Viscosity

The viscosity (η) of the CST19-04 glass melt was measured as a function of temperature with a fully automated Anton Parr FRS 1600 Furnace Rheometer System according to the PNNL procedure *High-Temperature Viscosity Measurement Using Anton Paar FRS1600* (EWG-OP-0046).[1] Approximately 200 g of the quenched glass was first crushed in a tungsten carbide mill and 25 to 30 mL (or ~70 g) of glass was placed into a Pt-alloy cylindrical cup. It was then heated to ~1150°C and maintained at that temperature until thermal equilibrium was reached. A Pt-alloy bob (spindle) was then lowered into the cup of molten glass. An initial torque reading (at a constant spindle speed) was taken at ~1150°C with subsequent measurements at targets of 1050°C, 950°C, 1150°C, 1250°C, and then 1150°C, in that order, to evaluate hysteresis. The glass required adjustment of the 1250°C target measurement temperature down to 1195°C due to melting temperature and volatility. The hysteresis approach to viscosity measurement allows for the potential impacts of crystallization (at lower temperatures) to be assessed (via reproducibility) with duplicate measurements being taken at approximately the melt temperature (T_M). Also, volatilization (at higher temperatures) was minimized by measuring viscosity at temperatures above T_M near the end of the viscosity measurement sequence. The soak time was 30 min at each temperature. Prior to viscosity measurements, the test instrumentation was calibrated using a standard glass (Defense Waste Processing Facility [DWPF] Startup Frit) as discussed in the literature (Crum et al. 2012). These results are discussed in Section 3.4.

2.6 Electrical Conductivity

The EC of the CST19-04 glass melt was determined using an Anton Parr FRS 1600 Furnace Rheometer System high-temperature furnace and a Solartron impedance analyzer according to PNNL procedure *High-Temperature Electrical Conductivity Measurement* (EWG-OP-0047).[2] Platinum plates (1.3 in. long by 0.28 in. wide) were placed parallel to each other with a separation of 0.367 in. A 30-mL glass sample was used for conductivity measurement in a Pt-alloy crucible. Before measuring the EC of the glass melt, a cell constant was measured using two NIST (National Institute of Standards and Technology) standard conductivity solutions of 5000 and 10,000 μS/cm at 25°C. Two measurements were taken at intervals of ~ 5 min for each solution. The averaged values of the four readings were then used to calculate the cell constant. This cell constant was later used in the calculation of the conductivity of each glass melt. The conductivity was verified before and after measuring the glass with DWPF startup frit (Crum et al. 2012).

For glass measurements, the sample was first heated to melting temperature and the probe was slowly lowered into the molten glass to a depth of 12.7 mm. After the temperature was stabilized, a scan from 1 to 0.1 Hz in 3 min was conducted and resistance at 1 kHz was used to calculate the EC. After the glass was held at temperature for 10 min to ensure temperature stabilization, two scans were made. The EC was measured at four different temperatures in a range around the melting temperature of the glass. These results are discussed in Section 3.5.

[1] McCarthy BP. 2017. *High-Temperature Viscosity Measurement Using Anton Paar FRS1600*. EWG-OP-0046, Rev. 0, Pacific Northwest National Laboratory, Richland, WA. This document is internal to PNNL and is not publicly available.

[2] McCarthy BP. 2017. *High-Temperature Electrical Conductivity Measurement.* EWG-OP-0047, Rev. 0, Pacific Northwest National Laboratory, Richland, WA. This document is internal to PNNL and is not publicly available.

2.7 Product Consistency Test

PCT responses were measured at PNNL for quenched and CCC samples of glass CST19-04 using Method A of the standard ASTM International procedure *Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT)* (ASTM C1285). Also included in the PCT experimental test matrix and tested in triplicate were the Environmental Assessment (Jantzen et al. 1993) glass, the Approved Reference Material (Mellinger and Daniel 1984) glass, and blanks. Glass samples were ground, sieved to -100 +200 mesh, washed, and prepared according to the standard ASTM International procedure. The prepared glass was added to water in a 1 g to 10 mL ratio, resulting in a glass surface area-to-solution volume ratio of approximately 2000 m^{-1}. The vessels used were desensitized Type 304L stainless steel. The vessels were closed, sealed, and placed into an oven at 90 ±2°C for 7 days ±3 h.

After the 7-day PCT, the vessels were removed from the oven and allowed to cool to room temperature. The final mass of the vessel and the solution pH were recorded on a data sheet. Each test solution was then filtered through a 0.45-µm-size filter and acidified with concentrated, high-purity HNO_3 to 1 vol% to assure that the cations remained in solution. The resulting solutions were analyzed for Si, Na, B, and Li. Normalized release rates were calculated based on target compositions using the average of the logarithms of the leachate concentrations. These results are discussed in Section3.6.

2.8 Toxicity Characteristic Leaching Procedure

The TCLP analyses were conducted at SwRI on the quenched and CCC sample of the CST19-04 glass. Crushed glass samples were extracted using U.S. Environmental Protection Agency (EPA) procedure EPA SW-846 Method 1311 (EPA 1992). About 100 g were used for extraction according to the method. Particle size reduction was required for all samples. The extracts were digested according to EPA SW-846 Method 3010A (EPA 1992) for the remaining metals and were analyzed by ICP-AES EPA SW-846 Method 6010D (EPA 2018) for all the RCRA (Resource Conservation and Recovery Act) metals (As, Ag, Ba, Cd, Cr, Hg, Pb, Se) as well as B. All holding times were met. These results are discussed in Section 3.7.

3.0 Results and Discussion

This section describes the test results for the chemical composition analysis, centerline cooling, CF, secondary phase identification, viscosity, EC, PCT, and TCLP measurements for the test glasses.

3.1 Chemical Analysis of Glass Composition

The data in Table 3.1 compares the targeted glass CST19-04 composition with the analyzed composition and the percent difference. The composition analysis of the glass was performed as described in Section 2.2. Because only ICP-AES was performed, several analytes were not measured. However, the analytes that were measured were very close to the target values, indicating that the glass was batched correctly. The few analytes that were off by more than 10% (Ca, P, and Pb) were low enough that they were close to the detection limit and were hard to measure extremely accurately, resulting in the larger error.

Table 3.1. Comparison of Targeted and Analyzed CST19-04 Glass Compositions

Glass ID	CST19-04		
Component	Targeted (wt%)	Analyzed (wt%)	% Diff
Ag_2O	0.11	0.10	-7
Al_2O_3	12.51	12.20	-3
B_2O_3	18.03	18.14	1
CaO	0.12	0.14	18
CeO_2	0.05	--	--
Cs_2O	0.03	--	--
F	0.09	--	--
Fe_2O_3	2.44	2.48	2
Li_2O	3.91	3.85	-1
MnO	0.24	0.24	1
Na_2O	10.66	10.45	-2
Nb_2O_5	2.29	--	--
Nd_2O_3	5.62	--	--
NiO	0.05	0.05	0
P_2O_5	0.24	0.18	-24
PbO	0.04	0.02	-52
SiO_2	37.81	38.62	2
TiO_2	3.66	3.59	-2
ZrO_2	2.08	2.11	1
Total	**99.98**	--	--

3.2 Crystal Identification in Canister Centerline Cooling Glasses

This section presents and discusses the CF results from CCC glasses obtained using the methods discussed in Section 2.3. XRD scans of the CCC glass samples identified two primary crystal types—nepheline and sodium neodymium titanium niobium oxide (from the CST IX media). The crystal types and wt% crystallinity results are summarized in Table 3.2. See Appendix B for photos of CCC-treated glasses and Appendix C for XRD spectra obtained from them.

Table 3.2. Weight Percent Crystallinity and Identification of Crystals by XRD in CCC-Treated Glasses

Glass ID	Starting CCC Temp (°C)	Wt% Crystallinity	Crystal Phase Identification
CST19-01[(a)]	1150	73.7	Nepheline
		50.7	Sodium neodymium titanium niobium oxide
CST19-02	1150	41.2	Nepheline
		27.0	Sodium neodymium titanium niobium oxide
CST19-03	1150	33.0	Nepheline
CST19-04	1150	0	Amorphous

(a) Glass was 100% crystalline and the semi-quantitative analysis was more than 100%.

3.3 Crystal Fraction of Heat-Treated Glasses

This section presents and discusses the CF (C_T) results obtained using the methods discussed in Section 2.4. For each glass composition, specimens were prepared, and heat treated at 850°C, 950°C, 1050°C, and 1150°C.

All of the glasses except CST19-04 formed significant crystals at 950°C. The CST appeared to be forming most of the crystals (sodium neodymium titanium niobium oxide) in all the glasses, indicating that the maximum CST loading in the glass had been exceeded given the quantity and composition of the HLW glass. In CST19-01 with 21.5 wt% CST IX media, there was still significant formation of crystals from the CST IX media at 1150°C.

Nepheline ($(Na,K)AlSiO_4$) was also formed at the lower temperatures, which is typical in high-Al HLW glasses and limits the HLW loading of high-Al wastes (Vienna et al. 2013). Nepheline precipitation from HLW glass during cooling is a major concern because it will likely reduce the durability of the resulting glass by removing three moles of glass former oxides (one mole of Al_2O_3 and two moles of SiO_2) for every mole of Na_2O (Kim et al. 1995). These results are summarized in Table 3.3. See Appendix D for photos of CCC-treated glasses and Appendix E for XRD spectra obtained from them.

Table 3.3. Weight Percent Crystallinity and Identification of Crystals by XRD in Heat-Treated Glasses

Glass ID	Temp (°C)	Wt% Crystallinity	Crystal Phase Identification
CST19-01[(a)]	850	51.9 51.5	Nepheline Sodium neodymium titanium niobium oxide
CST19-02	850	37.2 37.4	Nepheline Sodium neodymium titanium niobium oxide
CST19-03	850	24.5 16.2	Nepheline Sodium neodymium titanium niobium oxide
CST19-04	850	2.5 1.2	Neodymium titanium oxide NbOPbTi
CST19-01	950	8.8 47.7	Nepheline Sodium neodymium titanium niobium oxide
CST19-02	950	0.06 27.9	Nepheline Sodium neodymium titanium niobium oxide
CST19-03	950	2.6	Sodium neodymium titanium niobium oxide
CST19-04	950	0	NA
CST19-01	1050	36.7	Sodium neodymium titanium niobium oxide
CST19-02	1050	13.0	Sodium neodymium titanium niobium oxide
CST19-03	1050	0	NA
CST19-04	1050	0	NA
CST19-01	1150	21.5	Sodium neodymium titanium niobium oxide
CST19-02	1150	0	NA
CST19-03	1150	0	NA
CST19-04	1150	0	NA

NA = not applicable
(a) Glass was 100% crystalline and the semi-quantitative analysis was slightly more than 100%.

3.4 Viscosity

This section presents and discusses the viscosity results obtained using the methods discussed in Section 2.5. The results of the viscosity measurements of glass CST19-04 are summarized in Table 3.4, showing an average value of 2.6 Pa-s at 1150°C. The WTP desired range of viscosity at 1150°C is between 2 and 8 Pa-s[1], indicating that this glass composition is within this desired range.

The data was fit to a model in the form of the Arrhenius equation:

$$\ln(\eta) = A + \frac{B}{T_K} \quad (3.1)$$

where A and B are independent of temperature and temperature (T_K) is in K (T(°C) + 273.15). Figure 3.1 shows the viscosity data fit to the Arrhenius equation with an R^2 of 0.9998. This shows that the viscosity

[1] Perez JM. 2006. "Practical and Historical Bases for a Glass Viscosity Range for Joule-Heater Ceramic Melter Operation." Email to JD Vienna, Dtd, Dec. 22, 2006, CCN: 150054, River Protection Project, Hanford Waste Treatment and Immobilization Plant, Richland, Washington.

of this glass is very linear and fits the Arrhenius equation well. The values for the A and B coefficients are -10.213 and 1.592, respectively.

Table 3.4. Measured η (Pa·s) Values Versus Actual Temperature (in the Sequence of Measurement) for Glass CST19-04

Setpoint (°C)	Viscosity (Pa·s)	1/(T+273.15) × 10,000, K^{-1}	ln(η) (Pa·s)
1150	2.59	7.027	0.9535
1050	6.12	7.558	1.8111
950	16.6	8.176	2.8094
1150	2.65	7.027	0.9727
1195	1.91	6.811	0.6467
1150	2.66	7.027	0.9796

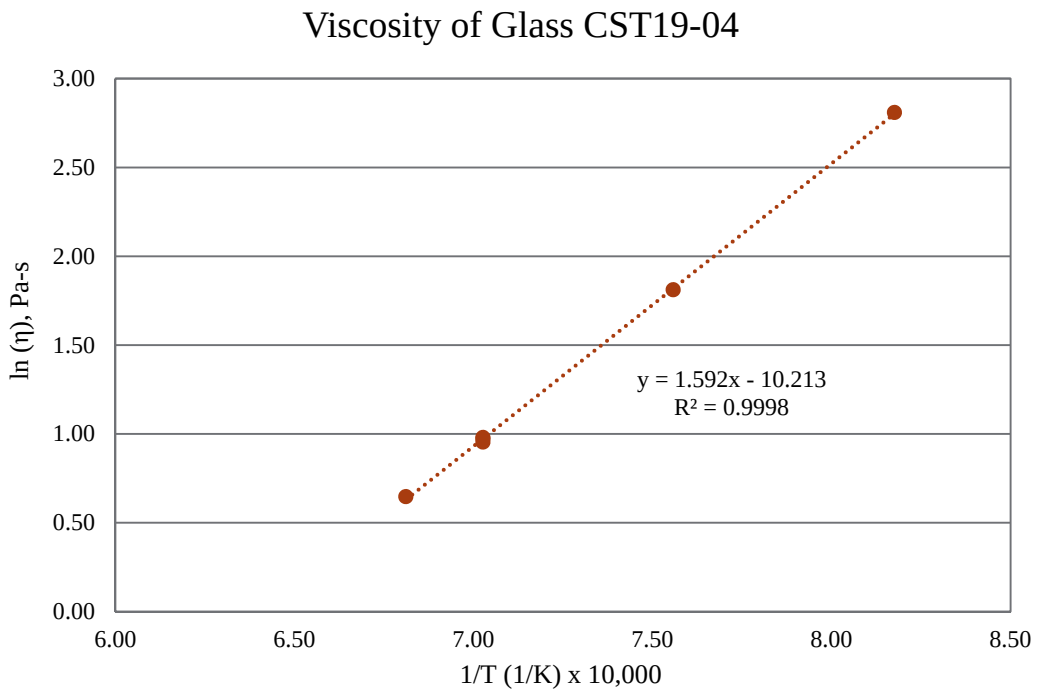

Figure 3.1. Viscosity-temperature data and Arrhenius equation fit for glass CST19-04.

3.5 Electrical Conductivity

This section presents and discusses the EC results obtained using the methods discussed in Section 2.6. Table 3.5 lists the EC versus temperature data for glass CST19-04 that is within the WTP desirable range of >10 S/m at 1100°C and <70 S/m at 1200°C (Vienna and Kim 2008). Figure 3.2 shows the plot for the ln (EC) versus temperature data for the CST19-04 glass obtained from the EC experiments fitted to the Arrhenius equation, which is shown below:

$$\ln(\varepsilon) = A + \frac{B}{T_K} \quad (3.2)$$

where *A* and *B* are independent of temperature and temperature (T_K) is in K (T(°C) + 273.15). The measured value at 1 kHz is plotted because it is the frequency used in the Arrhenius model and is closest to the real impedance. The EC of this glass is very linear and fits the Arrhenius model very well with an R^2 value of 0.9972. The values for the A and B coefficients are 7.8975 and -0.6169, respectively.

Table 3.5. Measured Electrical Conductivity (S/m) Values Versus Temperatures for the CST19-04 Glass

Temperature (°C)	Conductivity (S/m)	1/(T+273.15) x 10,000, K^{-1}	ln ε (S/m)
1050	25.91	7.558	3.255
1050	25.79	7.558	3.250
1150	35.57	7.027	3.572
1150	35.51	7.027	3.570
1196	39.15	6.807	3.667
950	17.21	8.176	2.846
950	17.09	8.176	2.838

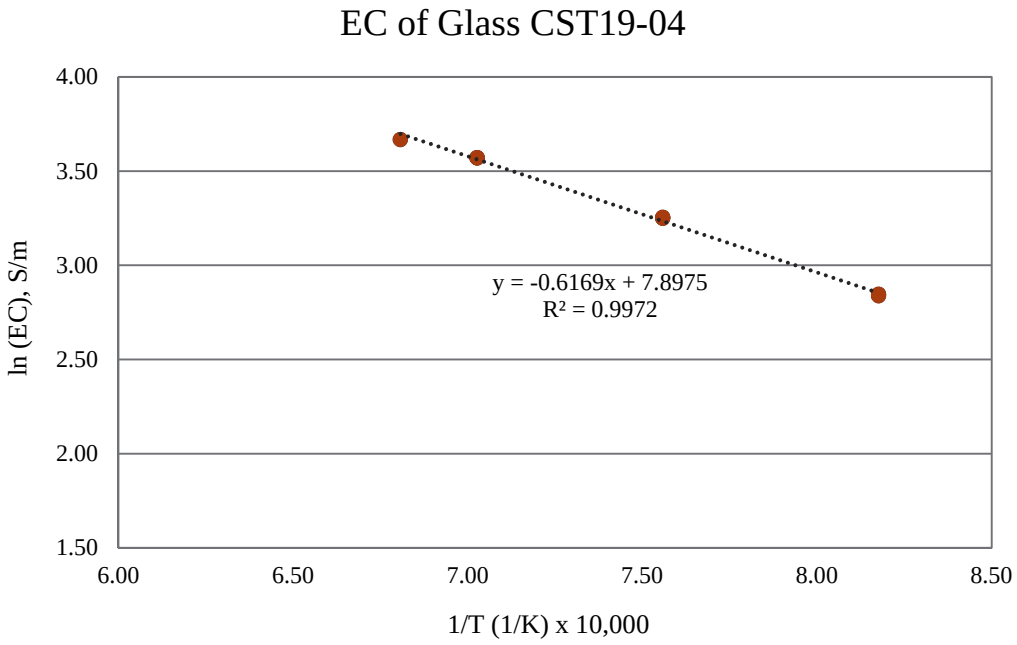

Figure 3.2. Electrical conductivity-temperature data and Arrhenius equation fit for glass CST19-04.

3.6 Product Consistency Test

This section presents and discusses the PCT results obtained using the methods discussed in Section 2.7 for the CST19-04 quenched and CCC-treated glasses. The normalization of the elemental release ratio of the element concentration to the surface area of the glass (NR) is typically used when reporting this result and reported as grams per square meter. This allows for comparison of tests conducted at different surface-area-to-volume ratios, materials having different densities, and samples having different particle

size fractions. The PCT results are summarized in Table 3.6. The NR of the WTP contract limit is the Environmental Assessment (EA) glass release limit (Jantzen et al. 1993) and is satisfied for both quenched and CCC-treated glasses.

Table 3.6. PCT Normalized Concentration Release Results for CST Glasses

Glass ID	Type	NR[B] (g/m^2)	NR[Li] (g/m^2)	NR[Na] (g/m^2)	NR[Si] (g/m^2)
CST19-04	Quenched	1.28	1.14	0.65	0.15
	CCC	1.22	1.11	0.62	0.17

3.7 Toxicity Characteristic Leaching Procedure

Table 3.7 lists the TCLP results obtained using the methods discussed in Section 2.8 for the CST19-04 glasses for quenched and CCC glasses. Both glasses completely passed the TCLP criteria for WTP Delisting Limit, RCRA Toxicity Limit, and RCRA Universal Treatment Standards (UTS) Limit. The Ag was above the RCRA UTS Limit, but the matrix spike criteria was not met, indicating that these values were higher than the actual values from the glass.

Table 3.7. TCLP Results for Samples of the CST Glasses

Sample ID	As (mg/L)	Ba (mg/L)	Cd (mg/L)	Cr (mg/L)	Hg (mg/L)	Pb (mg/L)	Se (mg/L)	Ag (mg/L)	B (mg/L)
CST19-04 Quenched	<0.025	<0.005	<0.005	<0.005	<0.0001	0.0194	<0.025	0.0288[(a)]	1.61
CST19-04 CCC	<0.025	<0.005	<0.005	<0.005	<0.0001	0.0202	<0.025	0.0356[(a)]	2.44
WTP Delisting Limit	3.08	100	0.48	5.00	2.00	5.00	1.00	3.07	--[(b)]
RCRA Toxicity Limit	5.00	100	1.00	5.00	0.20	5.00	1.00	5.00	--
RCRA UTS Limit	5.00	21	0.11	0.60	0.025	0.75	5.70	0.014	--

(a) Matrix spike and/or matrix spike duplicate criteria was not met.
(b) There is no limit for B.

4.0 Summary and Conclusion

The technical objective of this task was to conduct crucible-scale vitrification using non-radioactive CST IX media in a simulated HLW glass to determine test conditions, which could be applied to the vitrification of spent CST IX media used to process actual tank waste supernatants to remove Cs. Three glass compositions were prepared with the CST composition ranging from 10 to 21.5 wt% through modeling of the formulation using existing glass property models developed at PNNL by Vienna et al. (2016) trying to maximize the waste loading in the glass. The existing PNNL models do not include elemental constituents of the CST IX media. Therefore, they were augmented with the CST vitrification results available in the literature reports as well as CST loading characterization data. The glass formulation parameters included variable loadings of the sludge simulant, GFCs, and CST to identify formulations that minimized crystallinity in the molten glass upon slow cooling while simultaneously satisfying other glass property constraints.

Glass CST19-01 had to be melted at a temperature higher than the WTP can apply to form a glass. Then, after heat treating, it was primarily crystalline. Therefore, because of the high melting temperature required and the crystalline phase produced, it was decided to discontinue testing of this composition. Glasses CST19-02 and CST19-03 melted and formed glasses, however, upon heat treating and they formed significant crystals. It was decided to pursue preparation of these compositions using the simulant HLW sludge and CST IX media. These glasses behaved very similarly. Therefore, it was decided to not proceed with testing of these glasses and instead design a glass with a lower waste loading of 10% CST and 33% HLW sludge simulant and 57% glass forming chemicals that would melt well and not form crystals during heat treating. Glass CST19-04 was the only glass that, after melting twice at 1150°C, being treated with the CCC slow cool curve, and heat treating at 950°C for 24 h, formed no crystals. Therefore, it was decided to proceed with testing of this glass and not the others.

The glass viscosity measured data versus the temperature fit the Arrhenius equation quite well, producing a straight line with an R^2 value of 0.9998. At 1150°C, the viscosity was ~2.6 Pa-s, which is within the WTP desired range. The EC of this glass is very linear and fits the Arrhenius model very well with an R^2 value of 0.9972. At 1150°C, the EC was 0.355 S/cm, which is within the WTP desired range. The measured value at 1 kHz is used because this is the frequency used in the EC model and is closest to the actual impedance of the melter.

In measuring the CF of the CST19-04 glass by holding it at 950°C, 1050°C, and 1150°C for 24 ±2 h, it was determined that the glass had no crystals present. The previous glass compositions tested had significant nepheline and sodium neodymium titanium niobium oxide present. The CCC-treated CST19-04 glass was amorphous, whereas the previous glass compositions tested were similar to the measured CF and had significant nepheline and sodium neodymium titanium niobium oxide present.

PCT data showed that the CST19-04 glass has normalized release values for boron (1.28 and 1.22 g/m^2 for quenched and CCC, respectively) and sodium (0.65 and 0.62 g/m^2 for quenched and CCC, respectively) that are less than the WTP contract limit of the EA glass release limit for both the quenched and CCC heat-treated glass.

TCLP releases of As, Ba, Cd, Cr, Hg, Pb, Se, Ag, and B were determined for both quenched and CCC glasses by the SwRI. These results showed that both of these glasses passed the WTP Delisting Limit along the with RCRA limits. The Ag value was a little high, but that was most likely due to an error in the analysis as the matrix spike did not meet criteria.

This testing showed that CST can successfully be added to HLW glass and produce a glass that meets all durability and processing constraints. Overall, the first three glasses tested showed that the design was above the maximum loading of the CST in a glass of this formulation and was not able to produce glass. The fourth glass with lower waste loading was successfully incorporated into glass. However, based on tank waste composition, the waste loading of the glass may need to be varied to produce a successful glass.

5.0 References

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Appendix A – Quenched Glass Photographs

This appendix contains photos of glasses after they were melted the stated number of times at the temperature indicated in the figure caption. Each photo shows the ability of the composition to melt into an amorphous glass

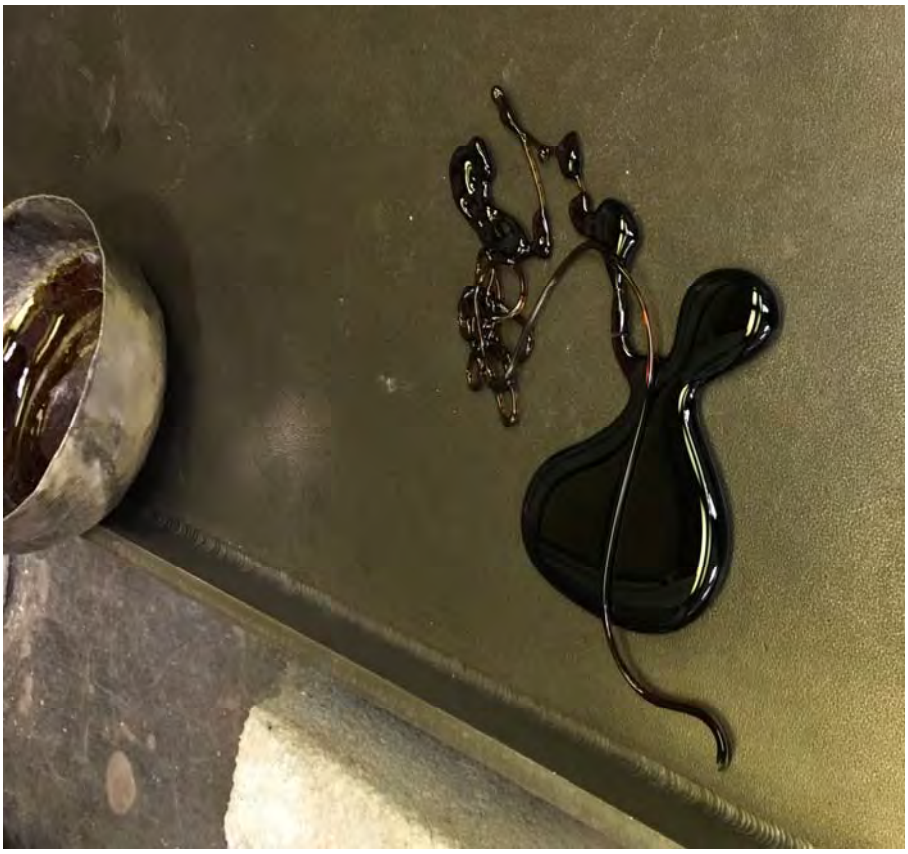

Figure A.1. Photograph of glass CST19-01 after melting fourth time at 1250°C.

Figure A.2. Photograph of glass CST19-02 after melting three times at 1150°C.

Figure A.3. Photograph of glass CST19-03 after melting twice at 1150°C.

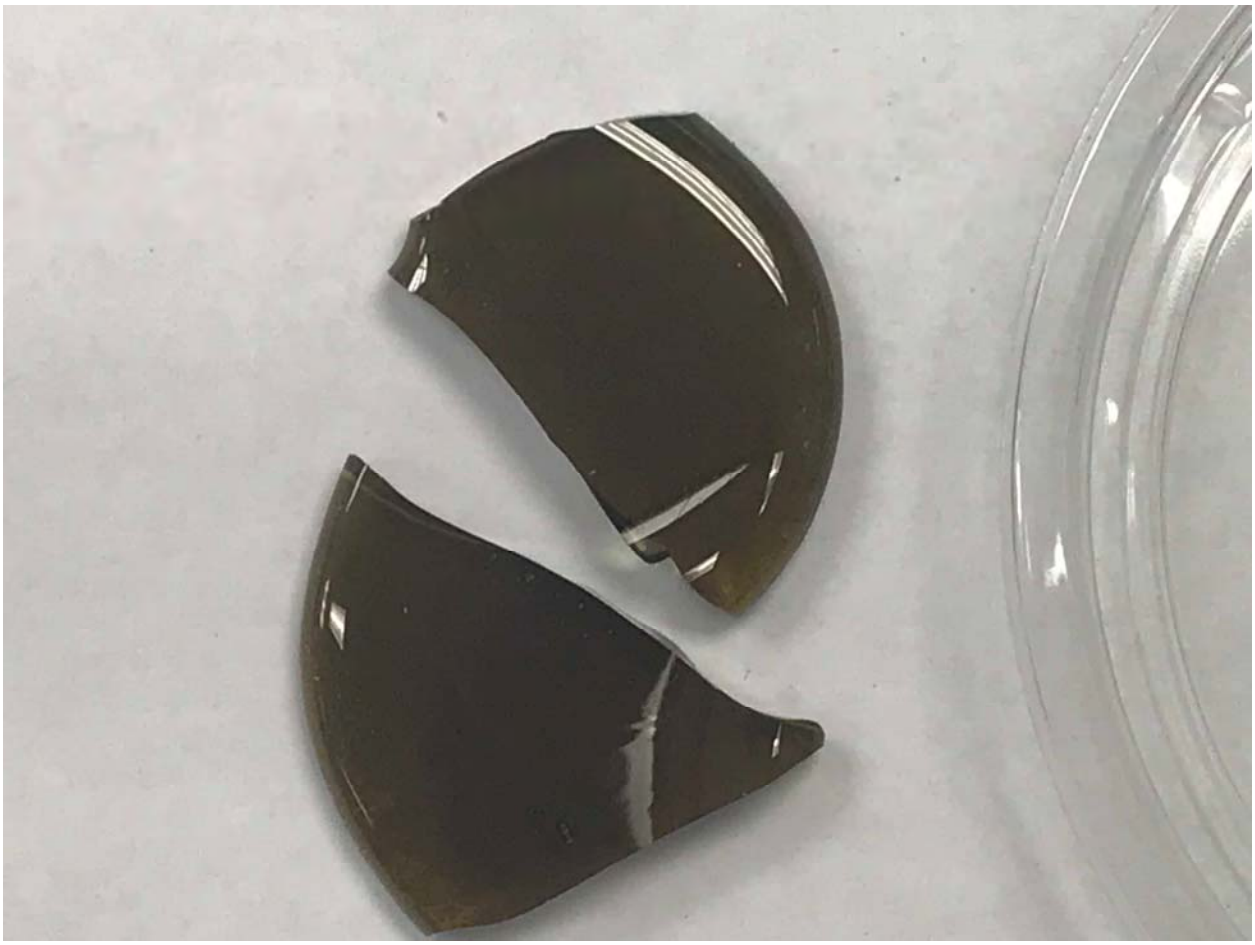

Figure A.4. Photograph of glass CST19-04 after melting twice at 1150°C.

Appendix B – Canister Centerline Cooled Glass Photographs

This appendix contains photos of glasses after they were canister centerline cooling (CCC)-treated beginning at the glass melting temperature, which is indicated in the figure captions. Each glass showed different responses to the CCC treatment as indicated by these photos.

Figure B.1. Photograph of glass CST19-01 after CCC beginning at 1150°C.

Figure B.2. Optical micrograph of glass CST19-01 after CCC beginning at 1150°C.

Figure B.3. Photograph of glass CST19-02 after CCC beginning at 1150°C.

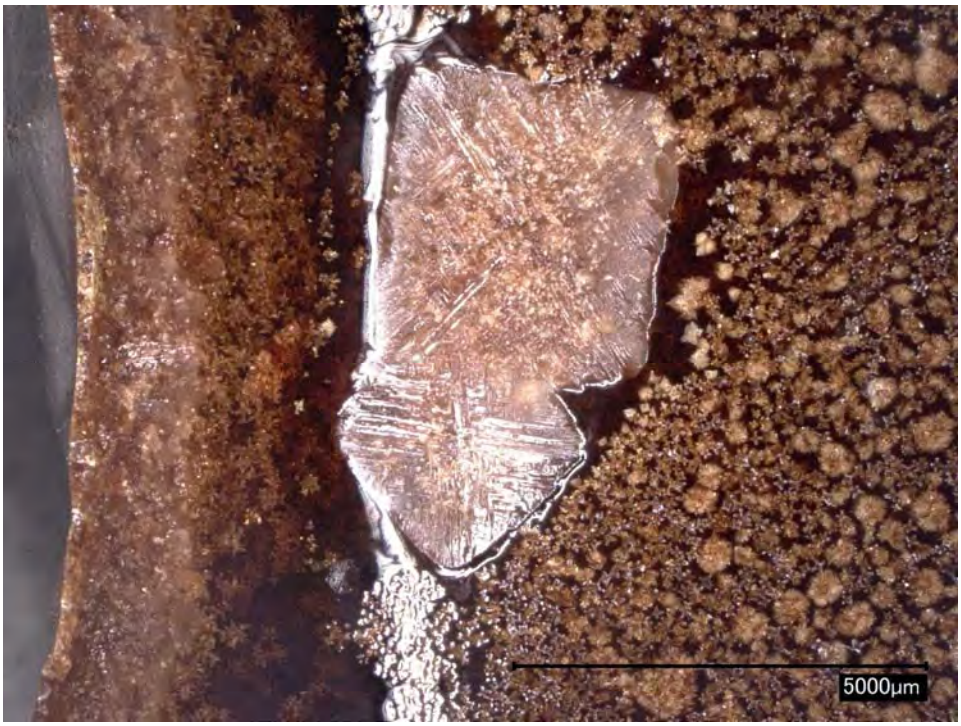

Figure B.4. Optical micrograph of glass CST19-02 after CCC beginning at 1150°C.

Figure B.5. Photograph of glass CST19-03 after CCC beginning at 1150°C.

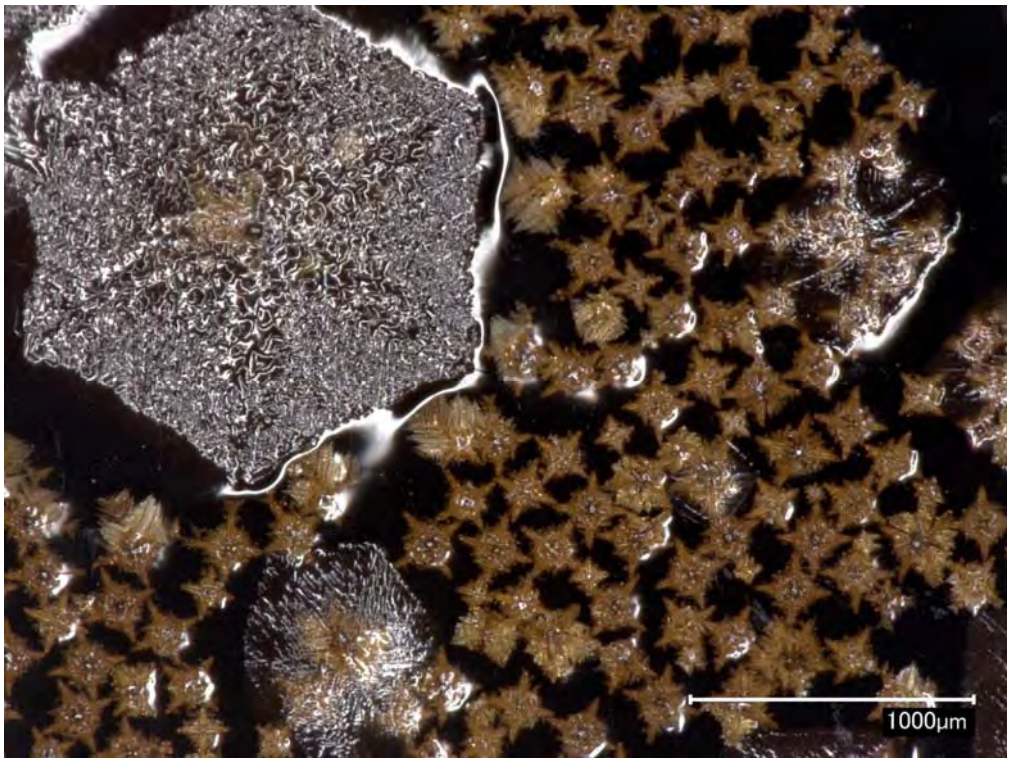

Figure B.6. Optical micrograph of glass CST19-03 after CCC beginning at 1150°C.

Figure B.7. Photograph of glass CST19-CST-04 after CCC beginning at 1150°C.

Appendix C – X-Ray Diffraction Spectra of Canister Centerline Cooling Treated Glasses

This appendix shows the X-ray diffraction (XRD) spectra of the test glasses after CCC treatment. These glasses all responded very differently to the CCC treatment, from remaining amorphous to developing quite a few crystals of various kinds as shown by the following plots. Some glasses did not contain enough crystals to perform XRD and therefore are not included in this appendix.

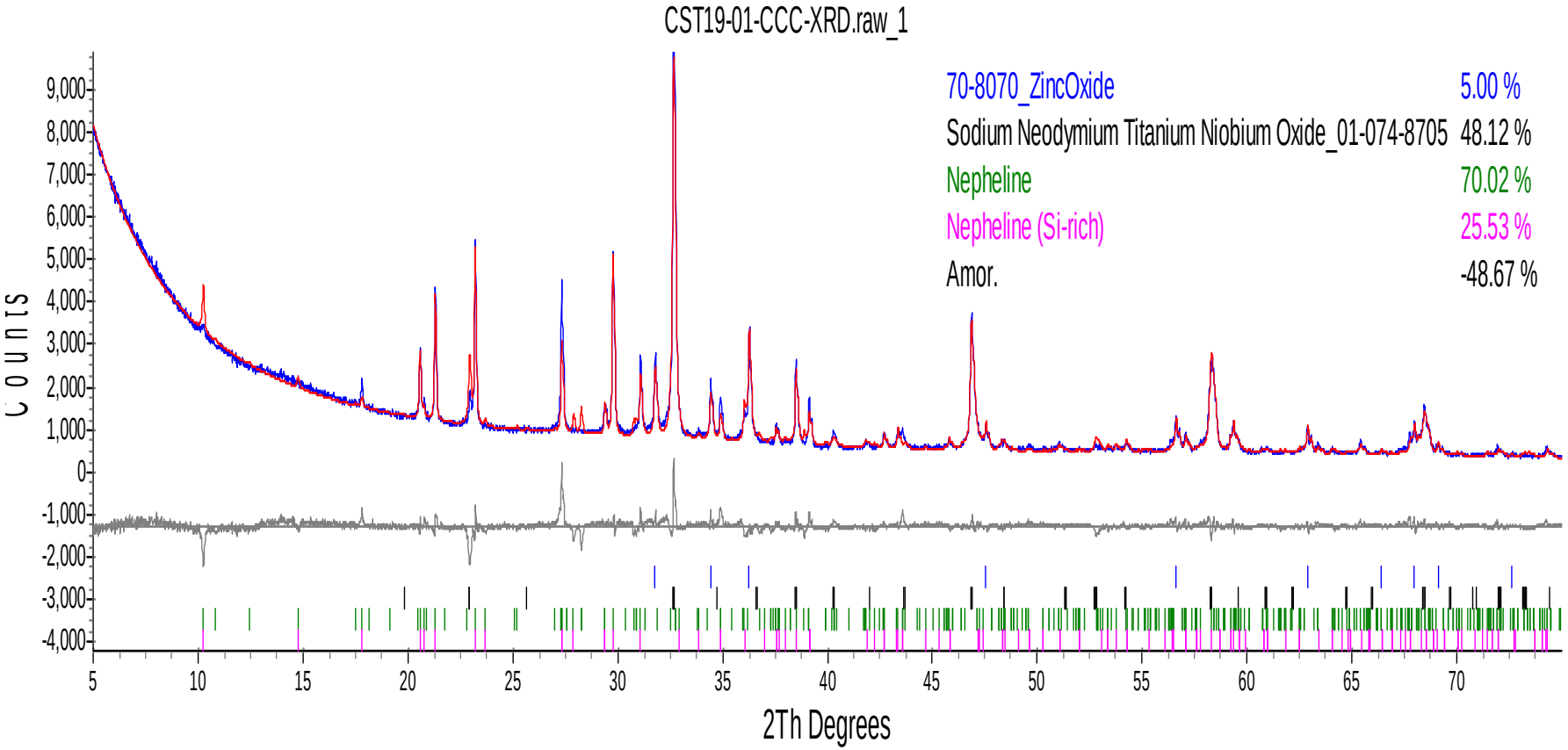

Figure C.1. XRD spectrum of CCC-treated glass CST19-01 (semi-quantitative for phases—100% crystalline).

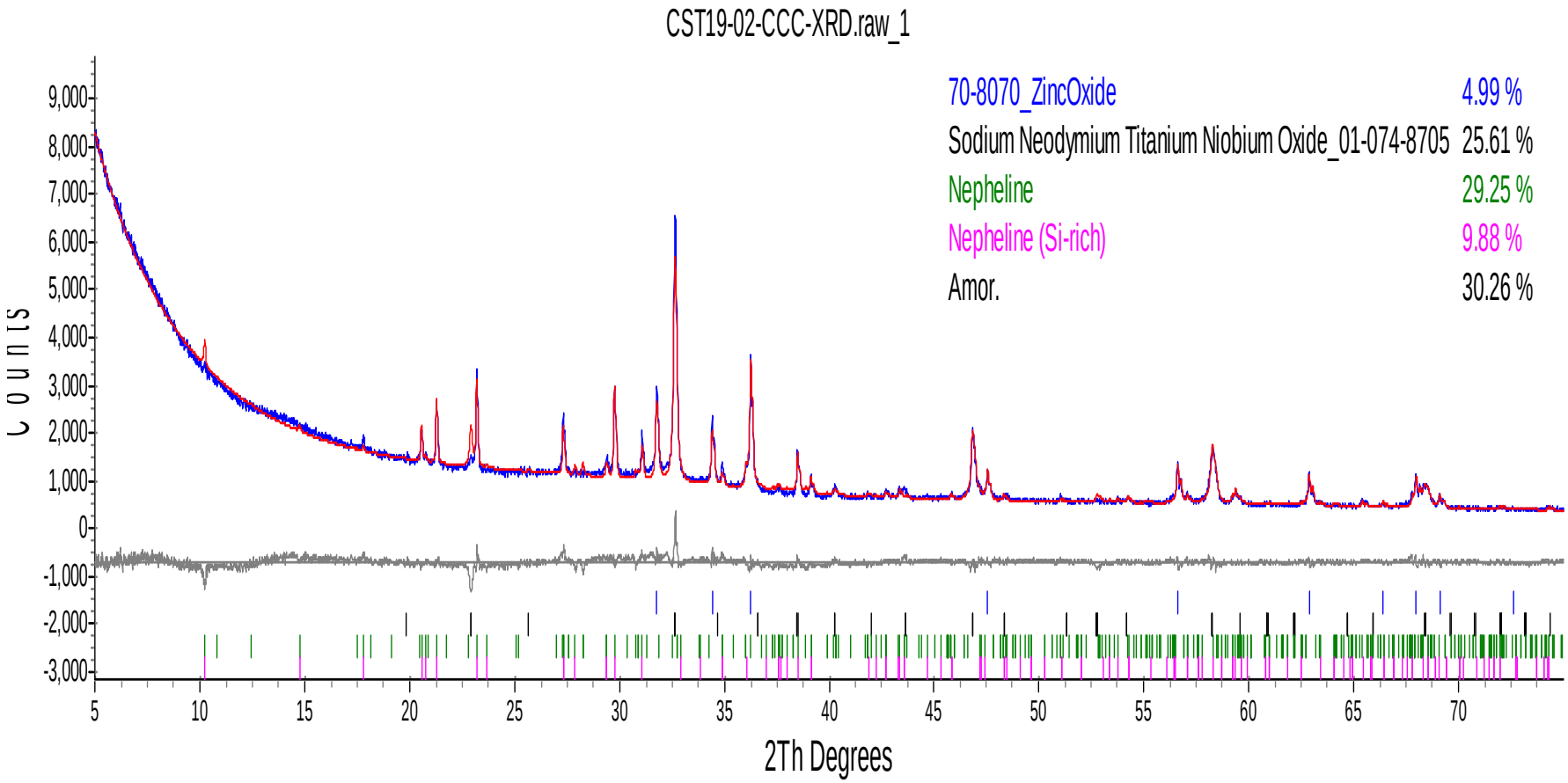

Figure C.2. XRD spectrum of CCC-treated glass CST19-02.

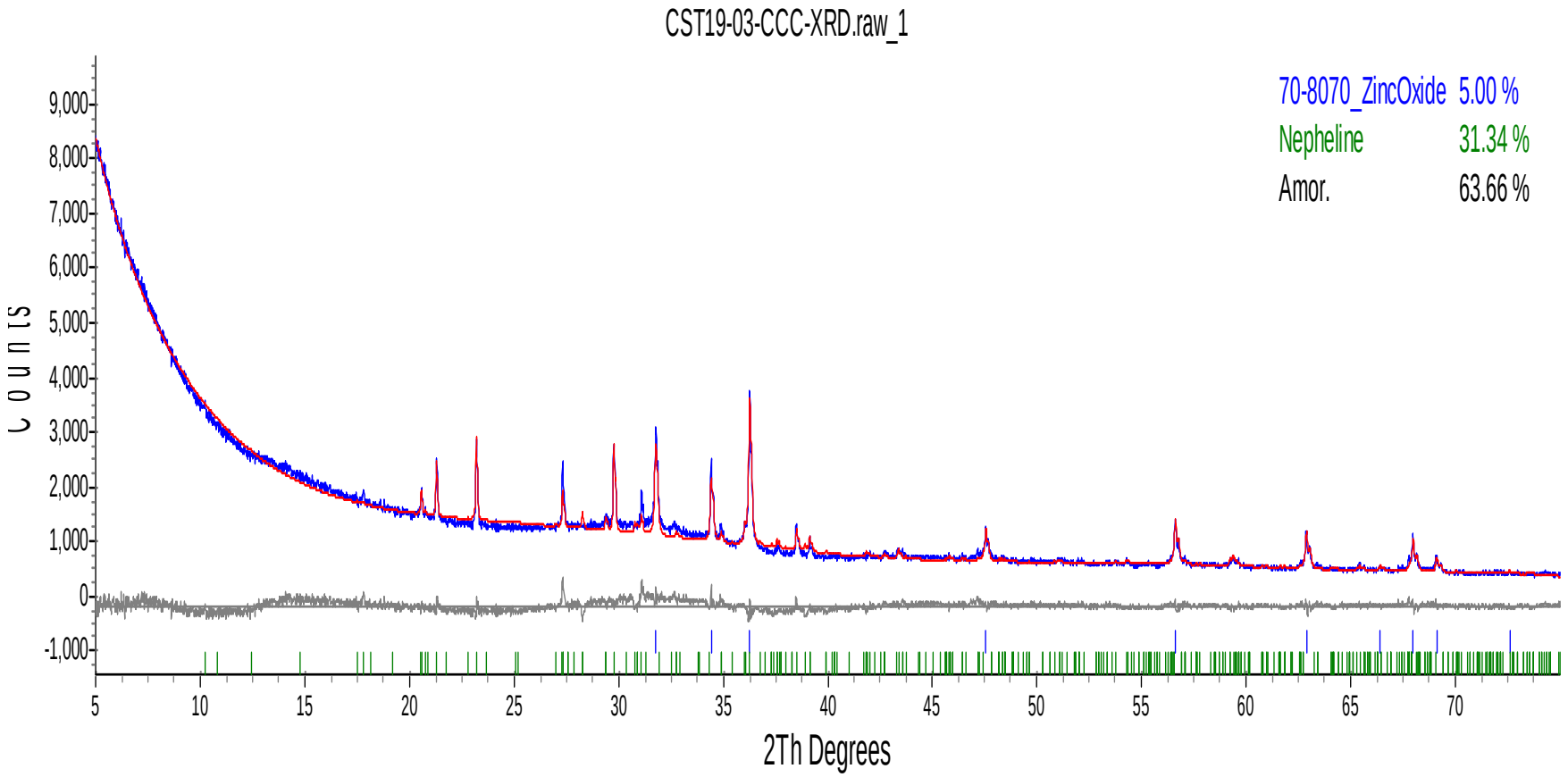

Figure C.3. XRD spectrum of CCC-treated glass CST19-03.

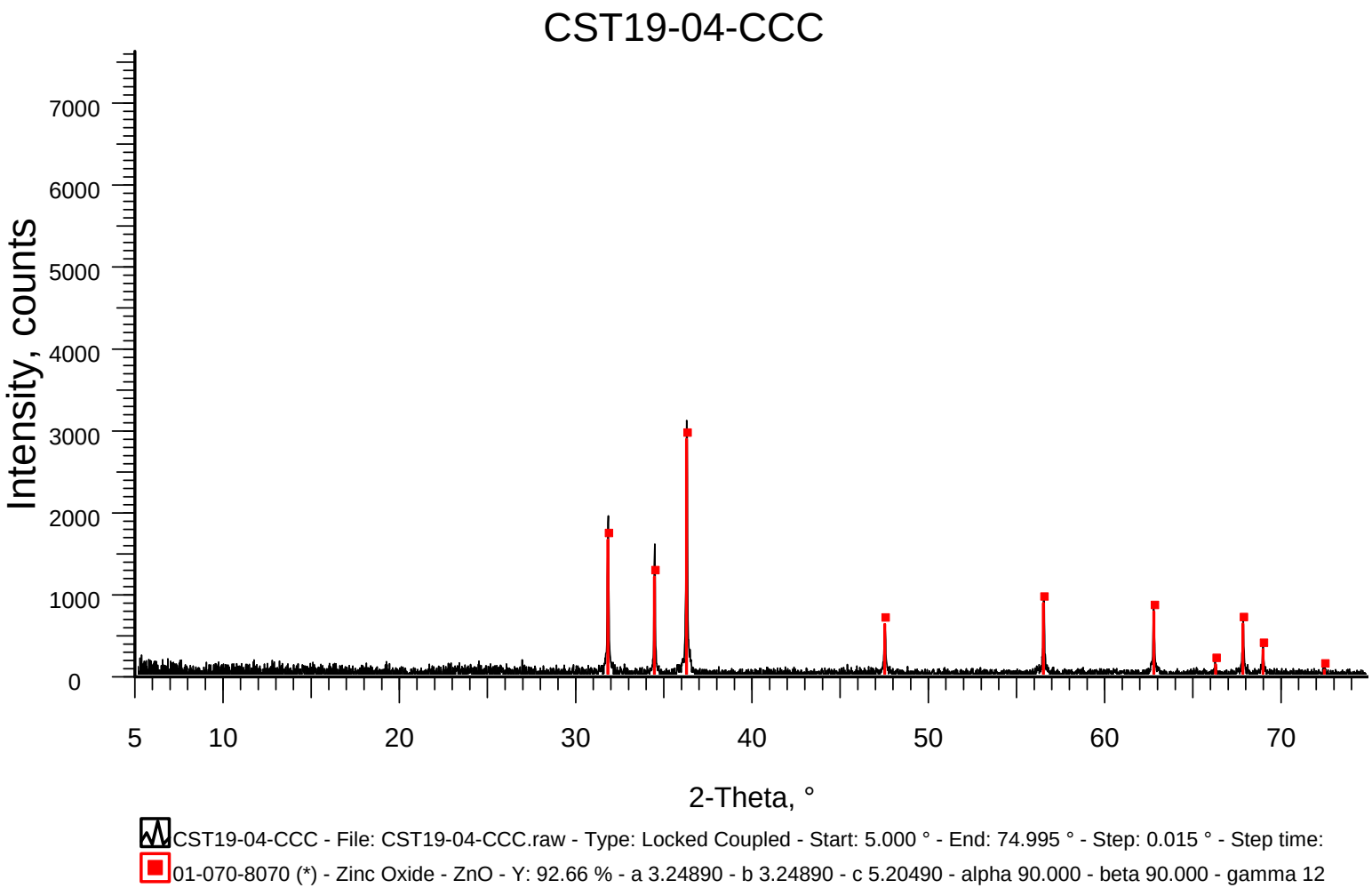

Figure C.4. XRD spectrum of CCC-treated glass CST19-04 (amorphous).

Appendix D – Crystal Fraction Glass Photographs

This appendix contains photos of glasses after they were held at various temperatures to test for crystal fractions. Each showed different responses to the hold temperatures as indicated by these photos.

Figure D.1. Photograph of glass CST19-01 after being held at 950°C for 24 hours.

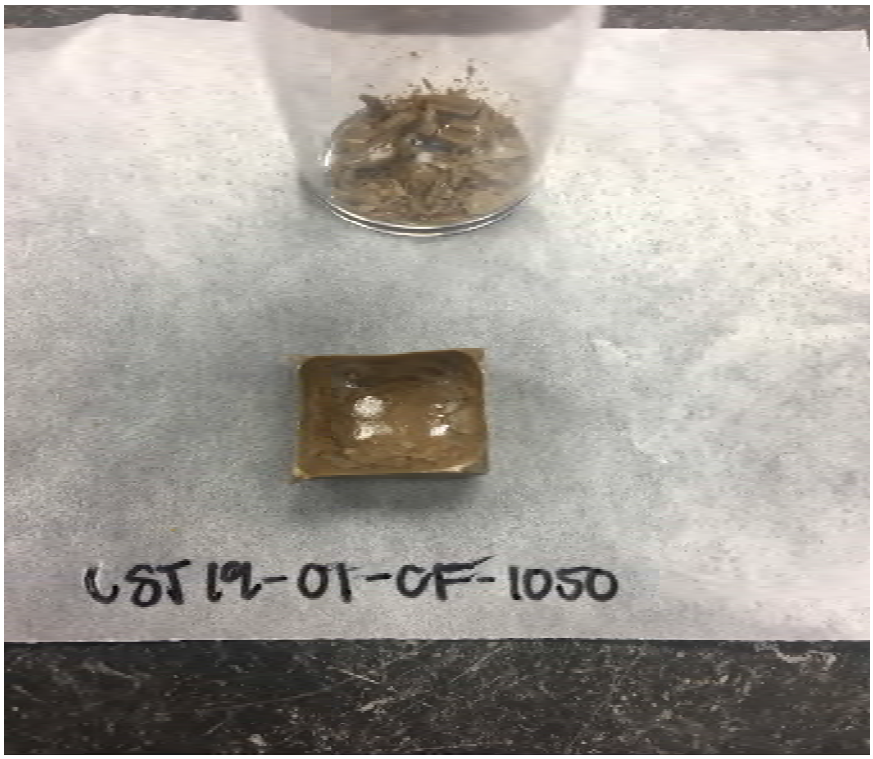

Figure D.2. Photograph of glass CST19-01 after being held at 1050°C for 24 hours.

Figure D.3. Photograph of glass CST19-02 after being held at 950°C for 24 hours.

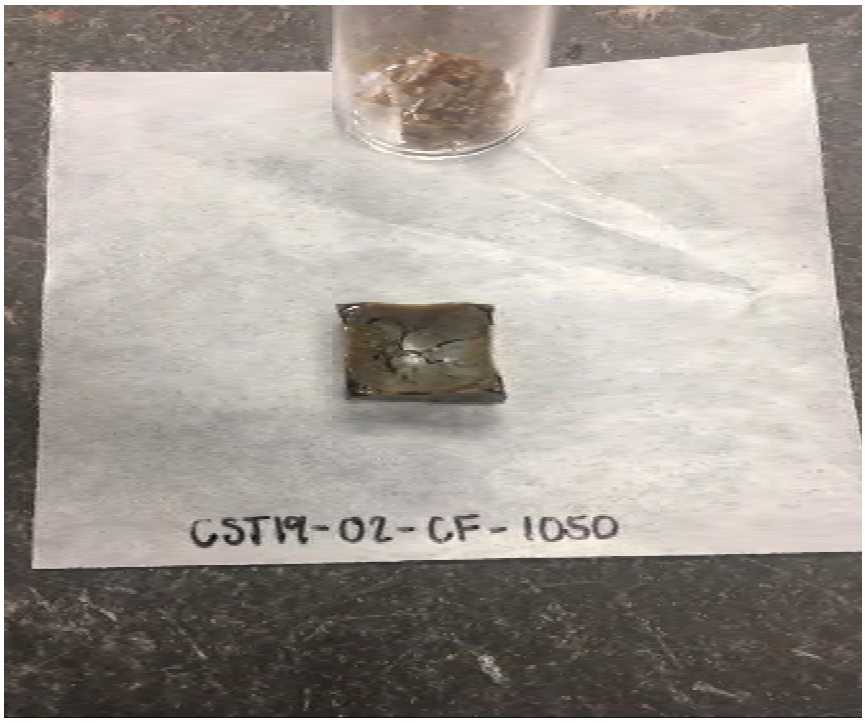

Figure D.4. Photograph of glass CST19-02 after being held at 1050°C for 24 hours.

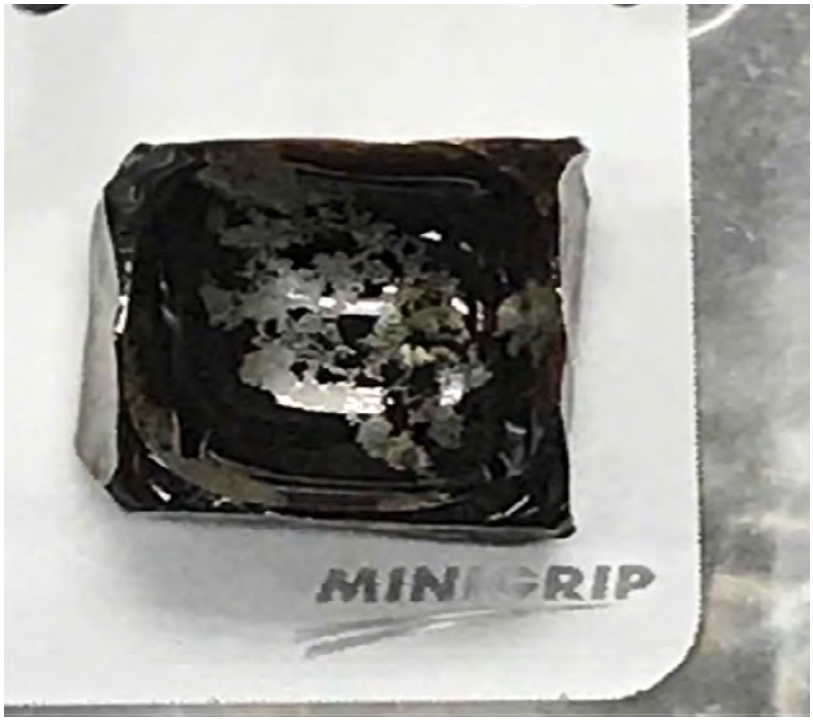

Figure D.5. Photograph of glass CST19-03 after being held at 950°C for 24 hours.

Figure D.6. Photograph of glass CST19-04 after being held at 850°C for 24 hours.

Figure D.7. Photograph of glass CST19-04 after being held at 950°C for 24 hours.

Figure D.8. Photograph of glass CST19-04 after being held at 1050°C for 24 hours.

Appendix E – X-Ray Diffraction Spectra of Crystal Fraction Tested Glasses

This appendix shows the X-ray diffraction (XRD) spectra of these glasses after crystal fraction (CF) testing. Some glasses did not contain enough crystals to perform XRD and therefore are not included in this appendix.

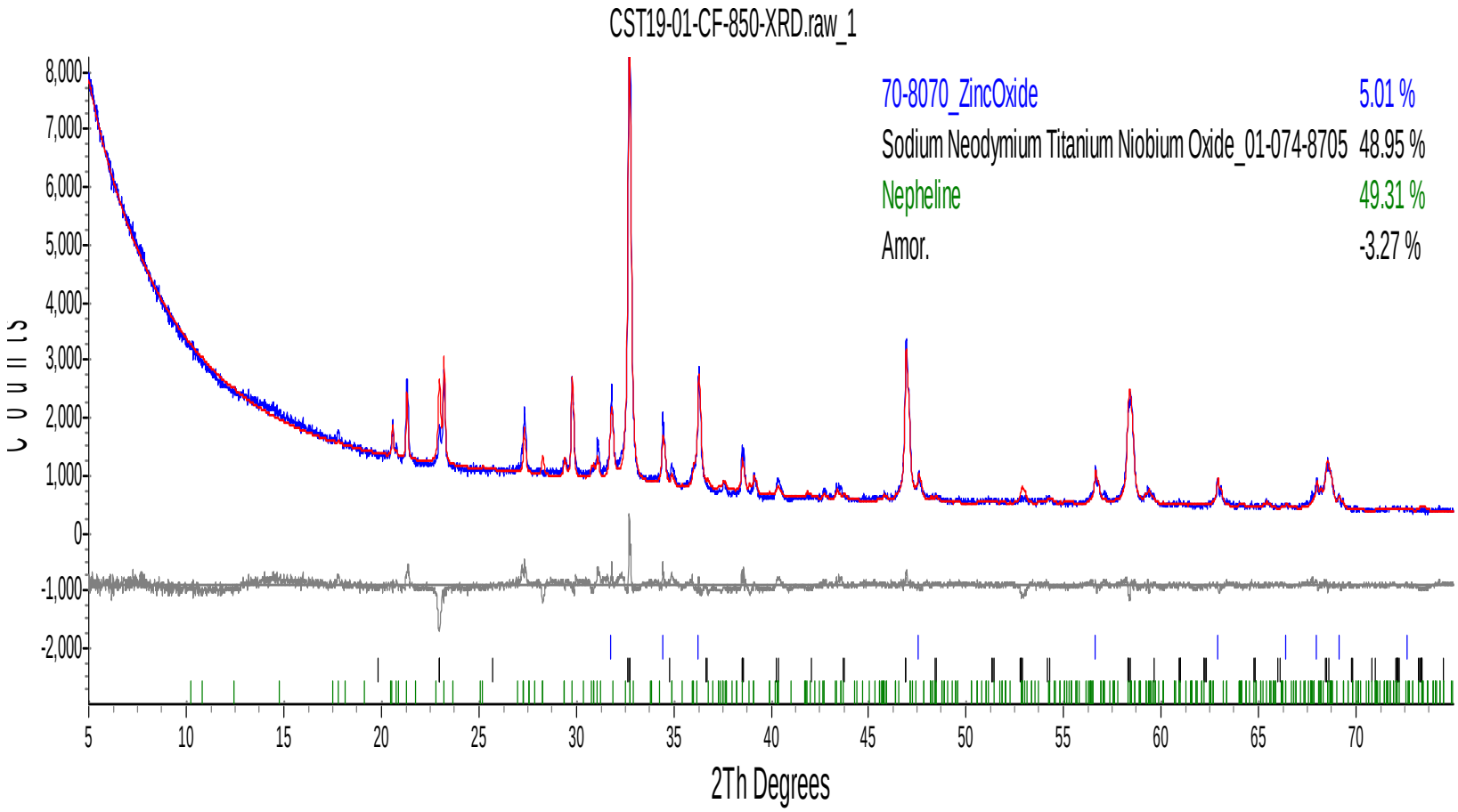

Figure E.1. XRD spectrum of CF tested glass CST19-01 after being held at 850°C for 24 hours (semi-quantitative for phases—100% crystalline).

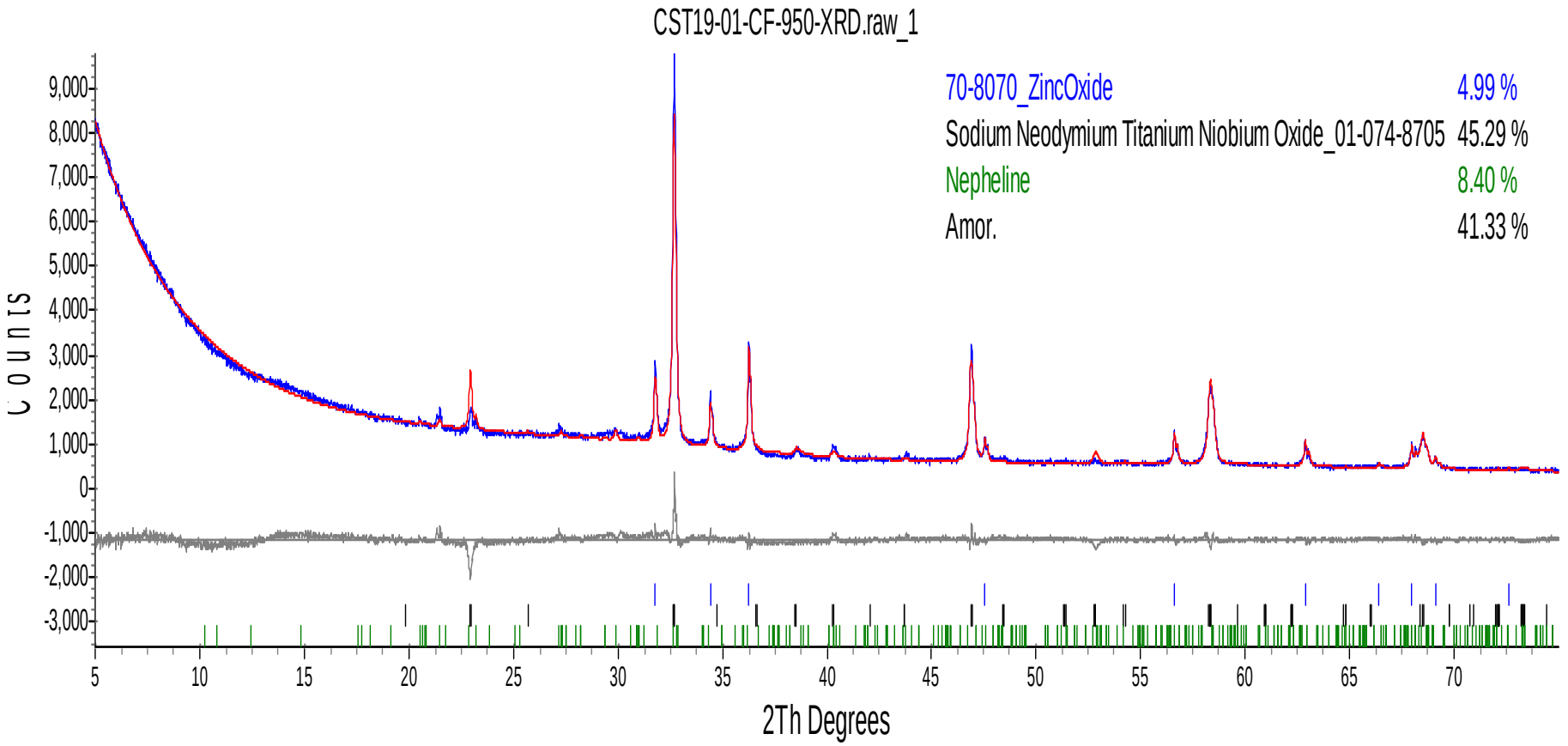

Figure E.2. XRD spectrum of CF tested glass CST19-01 after being held at 950°C for 24 hours.

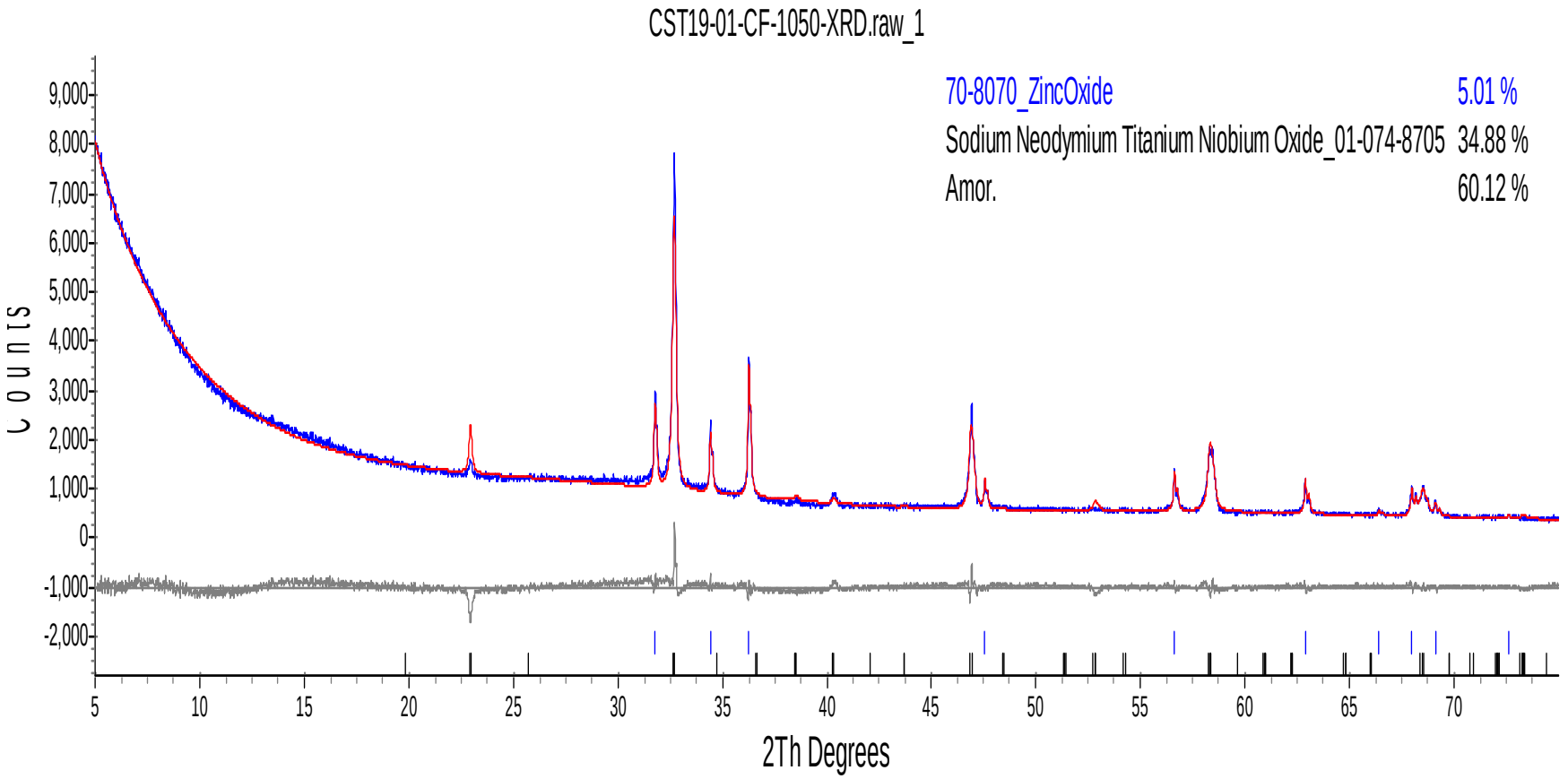

Figure E.3. XRD spectrum of CF tested glass CST19-01 after being held at 1050°C for 24 hours.

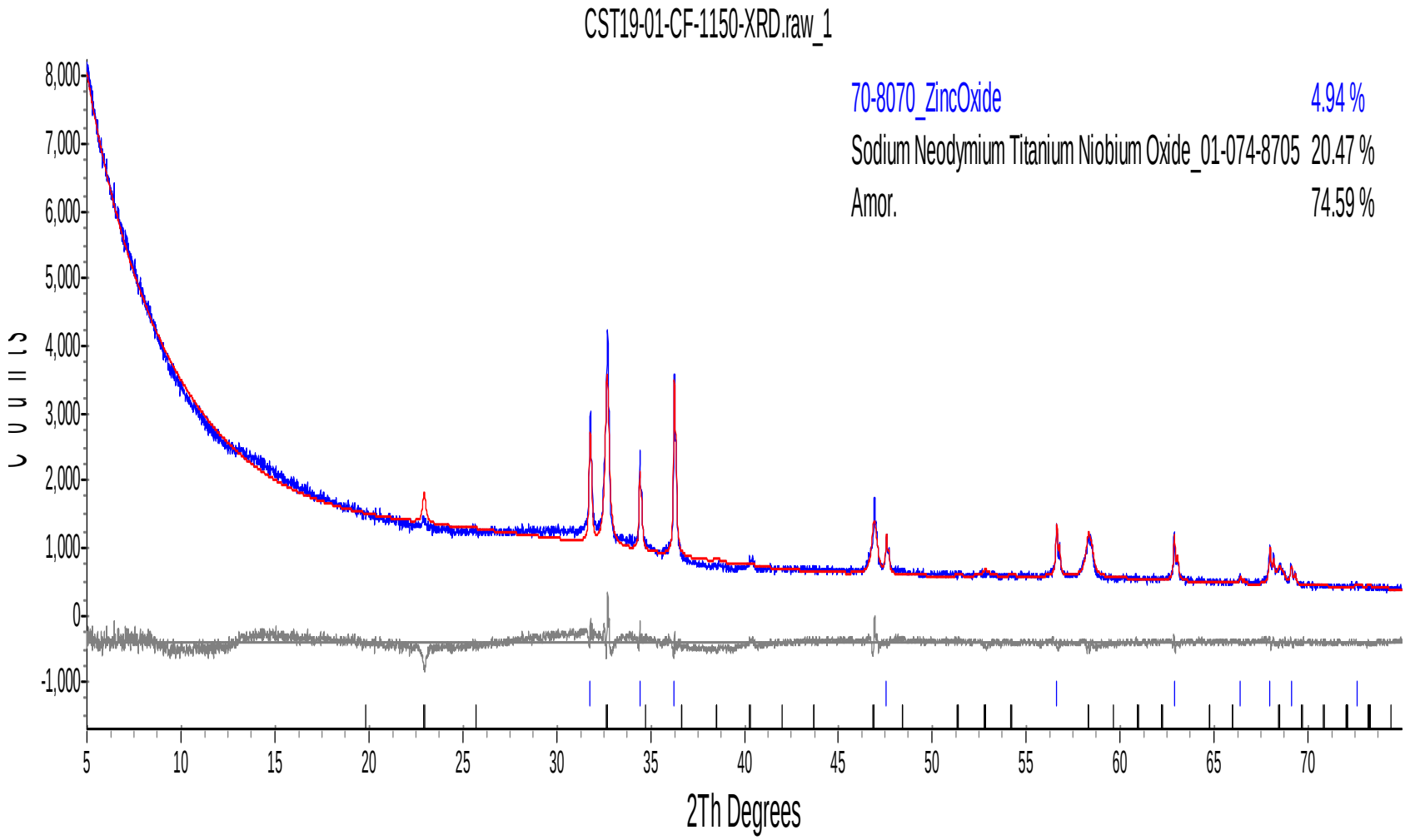

Figure E.4. XRD spectrum of CF tested glass CST19-01 after being held at 1150°C for 24 hours.

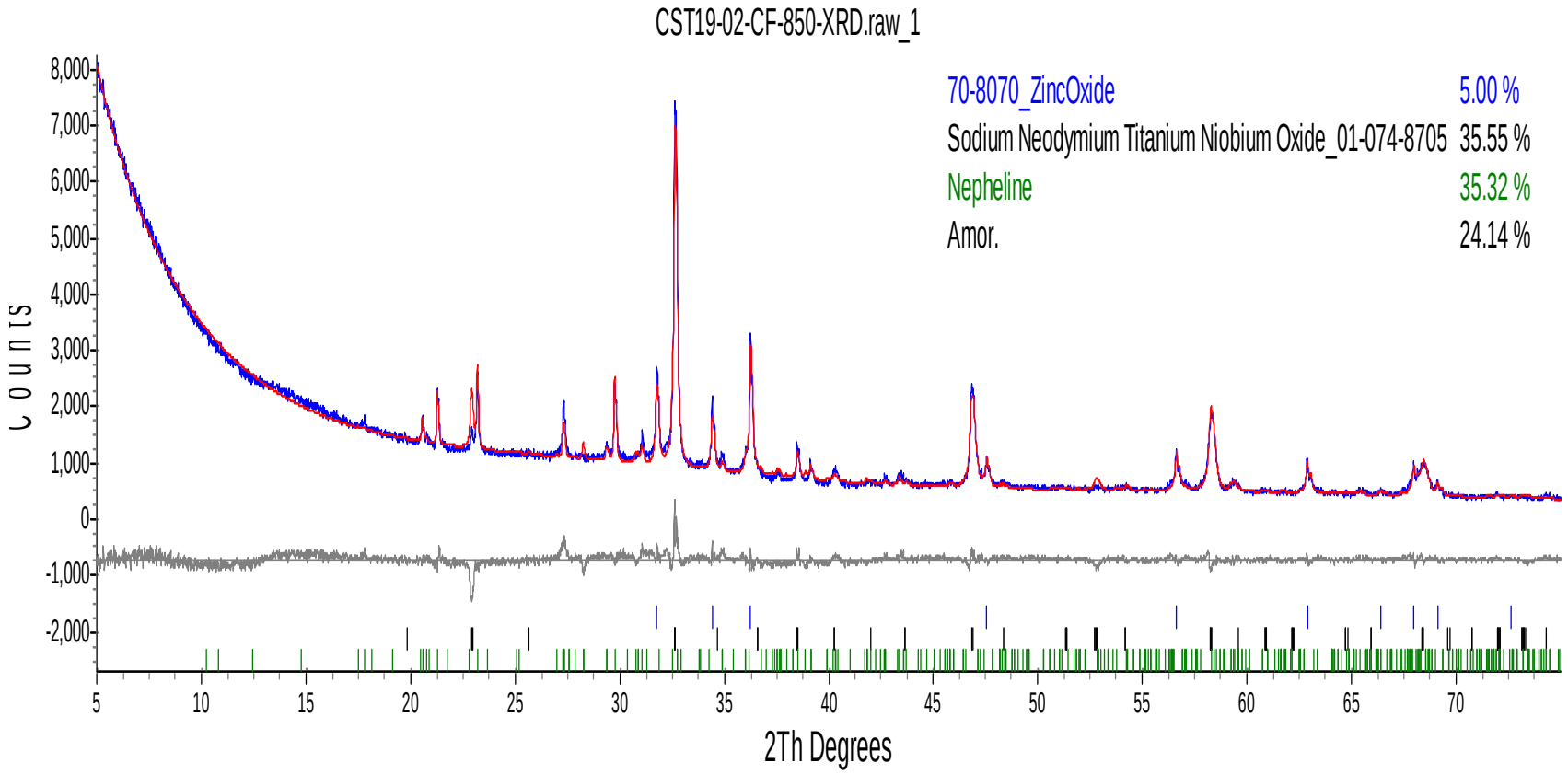

Figure E.5. XRD spectrum of CF tested glass CST19-02 after being held at 850°C for 24 hours.

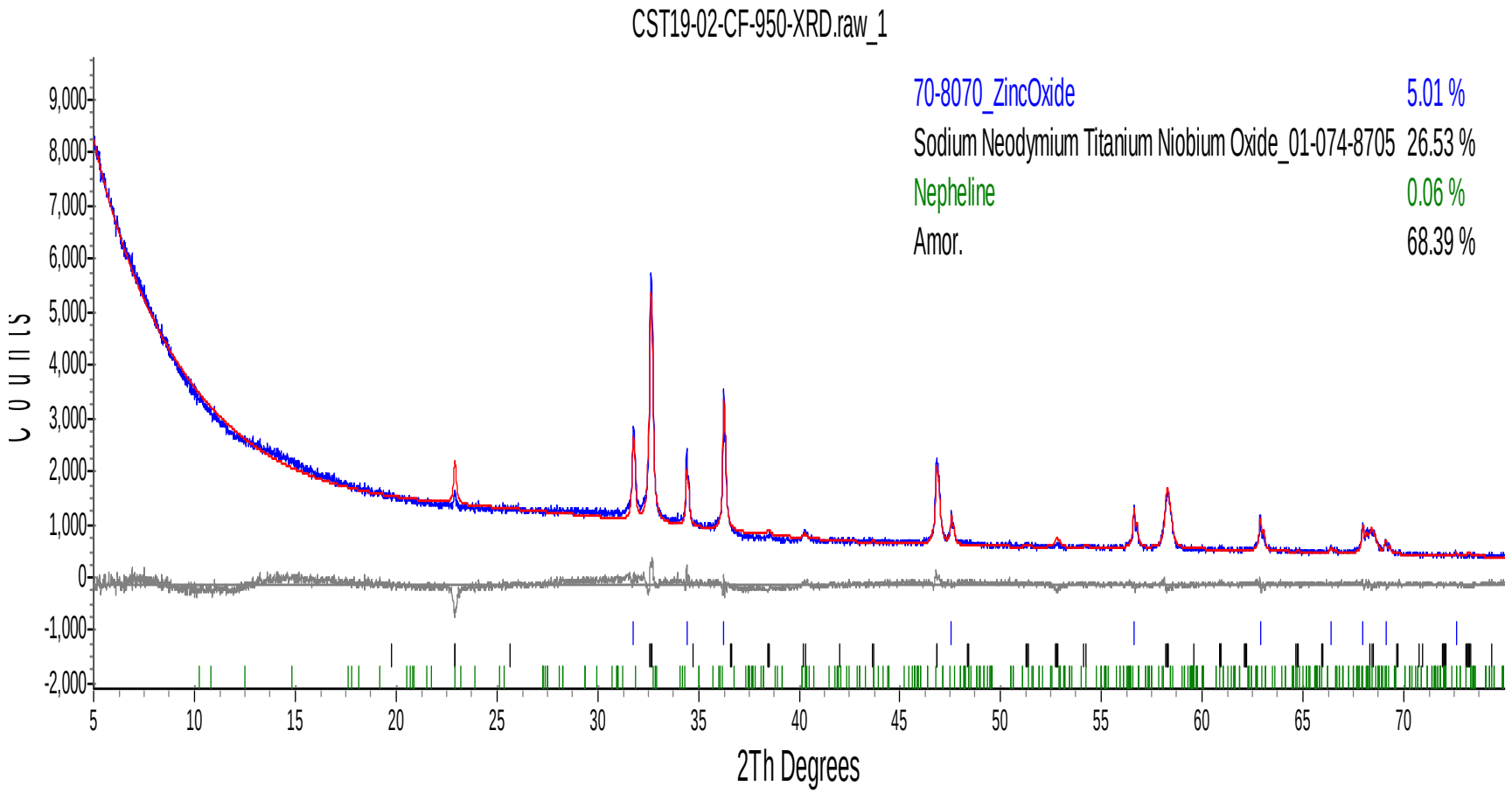

Figure E.6. XRD spectrum of CF tested glass CST19-02 after being held at 950°C for 24 hours.

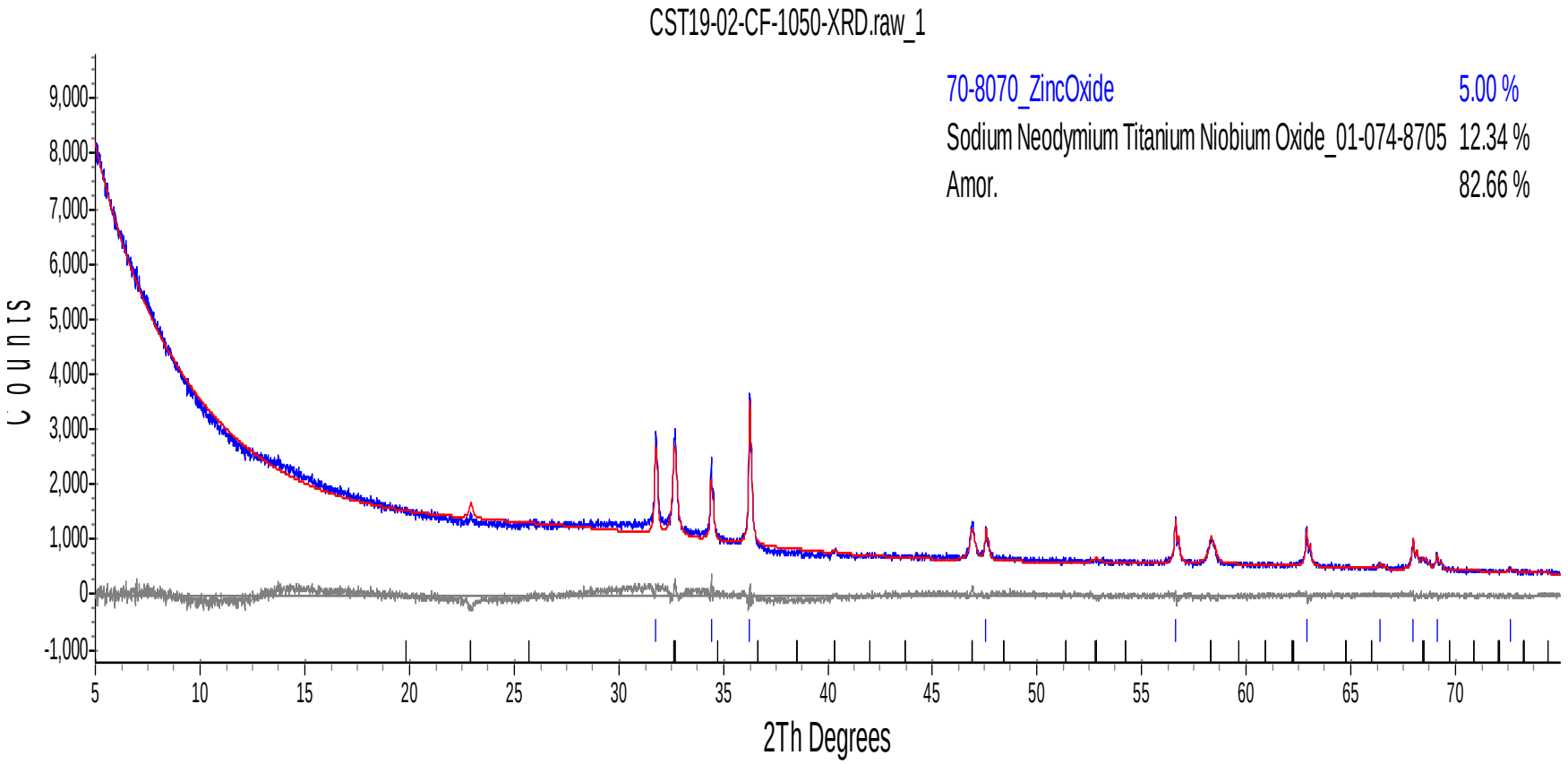

Figure E.7. XRD spectrum of CF tested glass CST19-02 after being held at 1050°C for 24 hours.

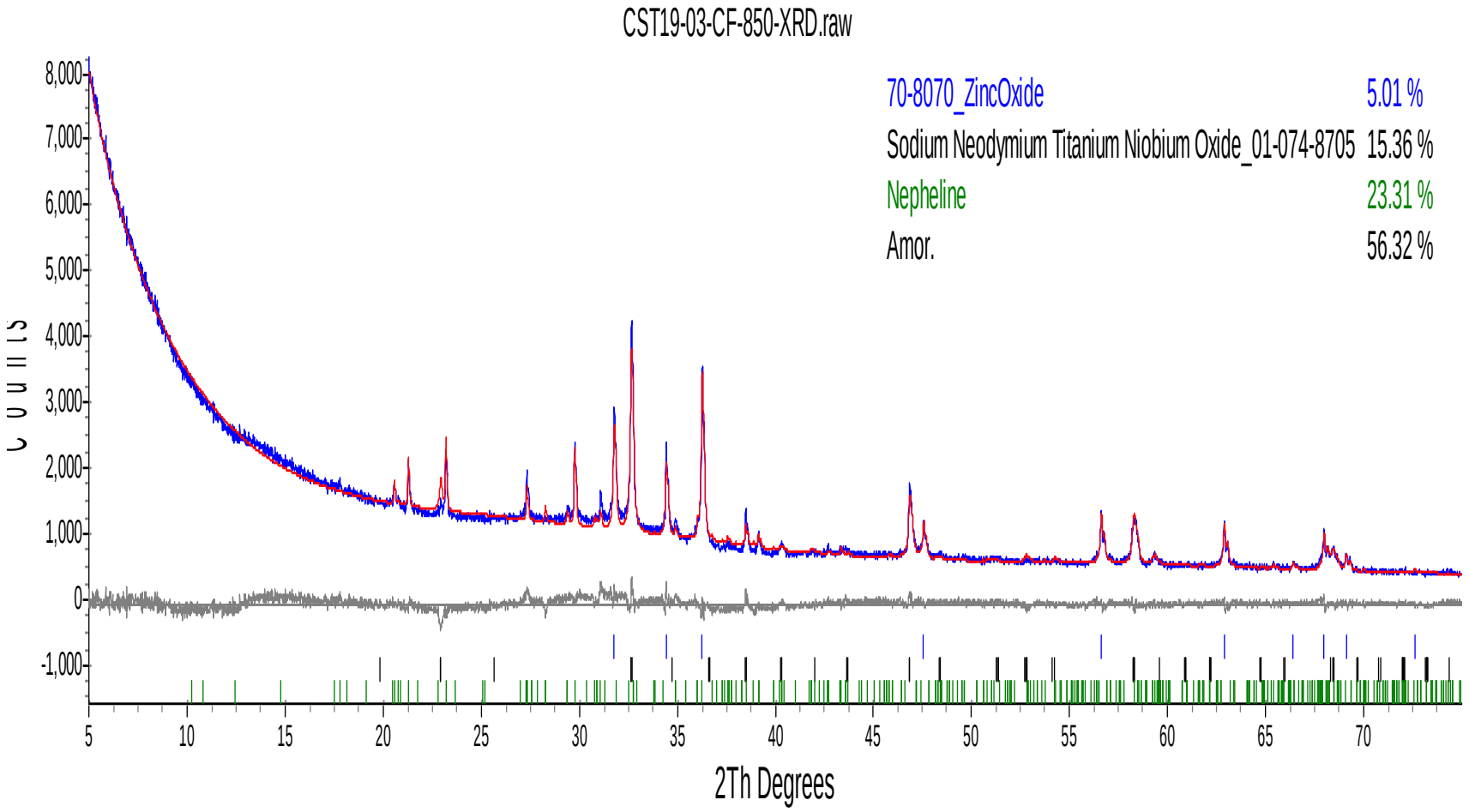

Figure E.8. XRD spectrum of CF tested glass CST19-03 after being held at 850°C for 24 hours.

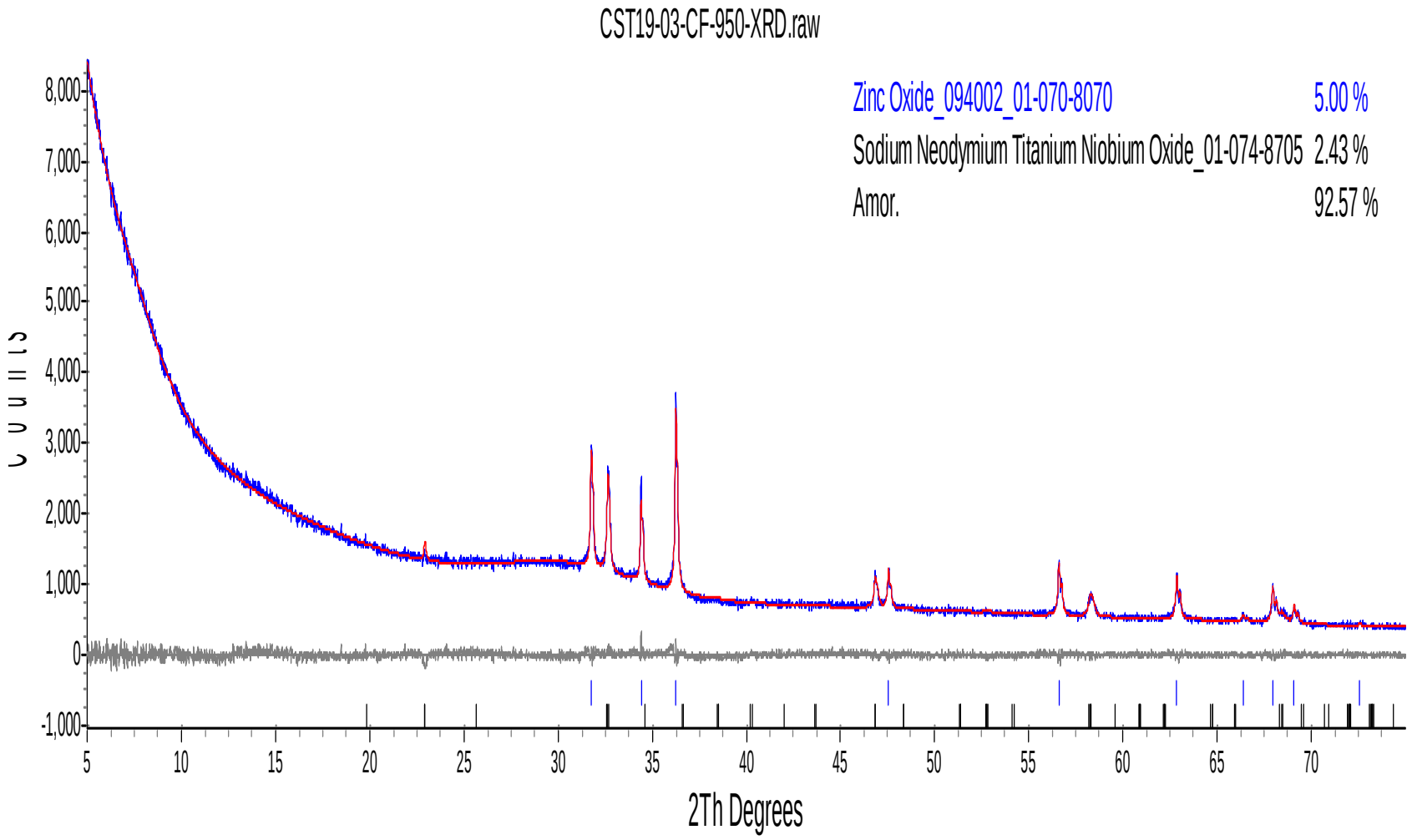

Figure E.9. XRD spectrum of CF tested glass CST19-03 after being held at 950°C for 24 hours.

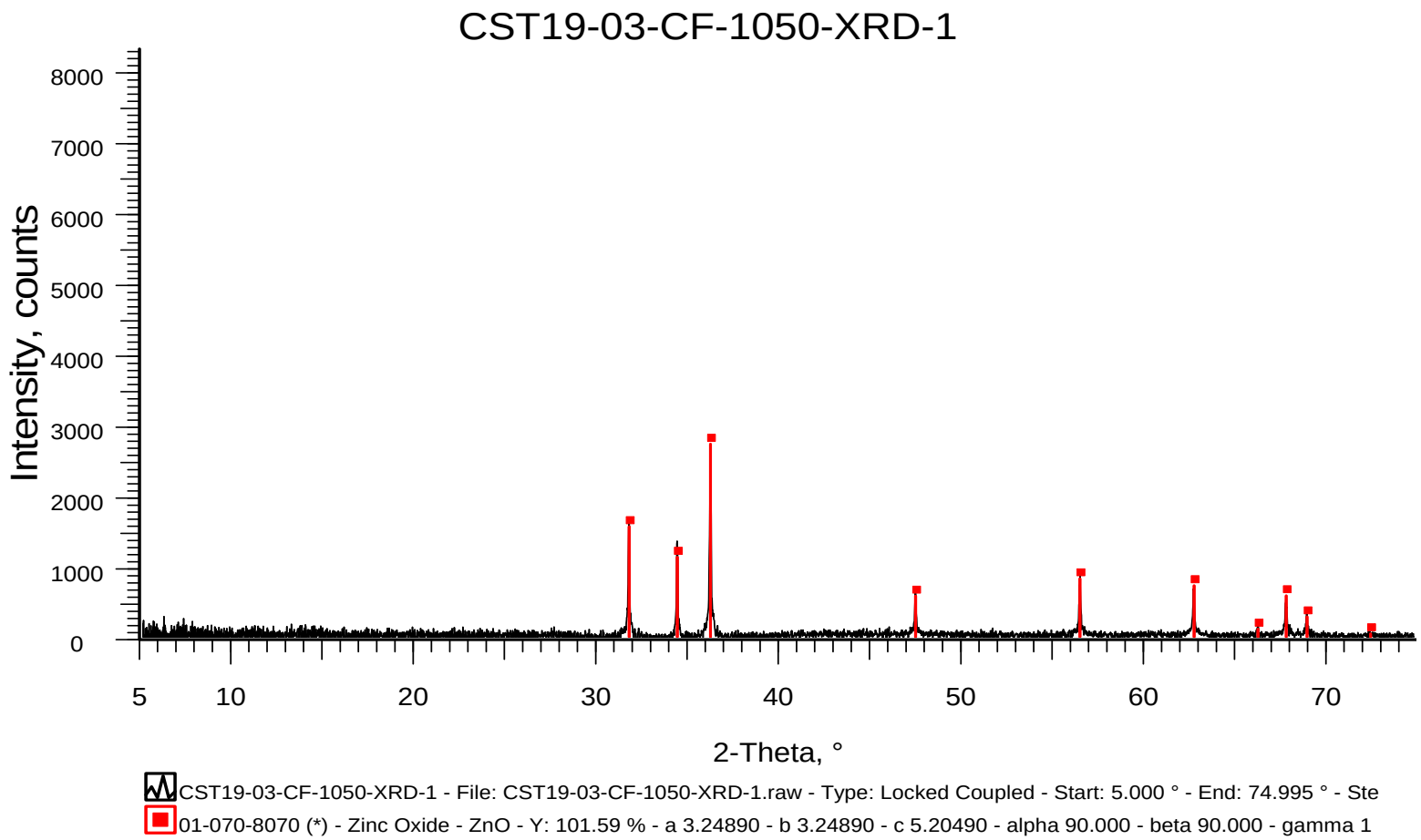

Figure E.10. XRD spectrum of CF tested glass CST19-03 after being held at 1050°C for 24 hours (amorphous).

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