EUROPEAN COMMISSION

Community Research

RAPHAEL

Contract Number: 516508 (FI6O)

DELIVERABLE (D-BF3.12)

Author(s): **Eva de Visser - Týnová**

Reporting period: 01/01/2008– 31/12/2008

Date of issue of this report: 9/12/2008

Start date of project: **15/04/2005** Duration : **48 Months**

Project co-funded by the European Commission under the Euratom Research and Training Programme on Nuclear Energy within the Sixth Framework Programme (2002-2006)		
Dissemination Level		
PU	Public	
RE	Restricted to the partners of the RAPHAEL project	
CO	Confidential, only for specific distribution list defined on this document	**X**

Distribution list

Person and organisation name and/or group	Comments
W. VON LENZA (FZJ)	SP Leader
B. GRAMBOW (ARMINES)	WP Contact
E. DE VISSER – TÝNOVÁ (NRG)	WP Contact
BF partners	

ReActor for Process heat, Hydrogen And ELectricity generation (RAPHAEL)		
Sub-project: SP-BF **Work package:** 3	**RAPHAEL document no:** RAPHAEL-0812-D-BF3.12	**Document type:** D
Issued by: NRG **Internal no.:** RAPHAEL-D-BF3.12		**Document status:** Final

Document title

Screening study on the interaction between ZrC/SiC and fission products, viz. Ag and Cs

Executive summary

This report describes work related to the task 3.3 in WP-BF3. The aim of this work was to perform screening study on the interaction between ZrC/SiC and fission products (Ag, Cs). This study has been realized by using of HT XRD. Mixtures of carbides and suitable compounds of Ag/Cs have been made and studied at different temperatures and different atmospheres. No new phases coming out from the interactions between studied carbides and fission products have been detected at the tested conditions.

Revisions

Rev.	Date	Short description	Author	WP Leader	SP Leader	Coordinator
00	14/10/2008	First draft	E. de Visser Týnová NRG	J. Fachinger FZJ	W. von Lensa FZJ	E. Bogusch FANP
01	22/03/2010	Final	E. de Visser Týnová NRG	J. Fachinger FZJ	W. von Lensa FZJ	E. Bogusch FANP

Contents

1 Introduction

One of the very important tasks in the understanding of the possible behaviour of SiC and ZrC is studying the interaction between fission products and these carbides. Cs and Ag are among the fission products which may well come in contact with carbide layer. The interaction may result in the formation of new phases which may have a negative effect on the stability of the carbide layer. And thus its leaching behaviour. Knowledge of the carbide-FP system is therefore of utmost importance. Mixture of carbides and suitable Ag/Cs compounds have been heated and subsequently checked for their phase composition by X-ray diffraction (XRD). HT XRD has been employed to register possible phase transitions.
Relevant mixtures (depending on the outcome of this experimental work) will be then subjected to a leaching test in order to assess the effect of additional phase formation on the behaviour of the carbides.

2 Experimental part

2.1. Raw materials

This study has been done using the same commercial available chemical powders of SiC and ZrC as in the leaching studied as described in the deliverable D-BF3.2.

The used carbide powders have the following specifications:

- **Beta-SiC**: Alfa-Aesar, 99.8% (metals basis), $A_{spec.}$ = 12.91 m^2/gram
- **ZrC**: Alfa-Aesar, 99.5% (metals basis excluding Hf), Hf < 200 ppm, $A_{spec.}$ = 0.43 m^2/gram

The used nitrates to introduce the studied fission products have the following specifications:

- **$AgNO_3$**: Alfa Aesar, 99.8% (metal basis), melting temperature 212 ºC
- **$CsNO_3$**: Alfa Aesar, 99.8% (metal basis), melting temperature 414 ºC

All used raw materials have been checked by X- ray diffraction measurements, results of these analyses are depicted at following figures. Figures 2-1 to 2-4 show that all used powders are crystalline pure.

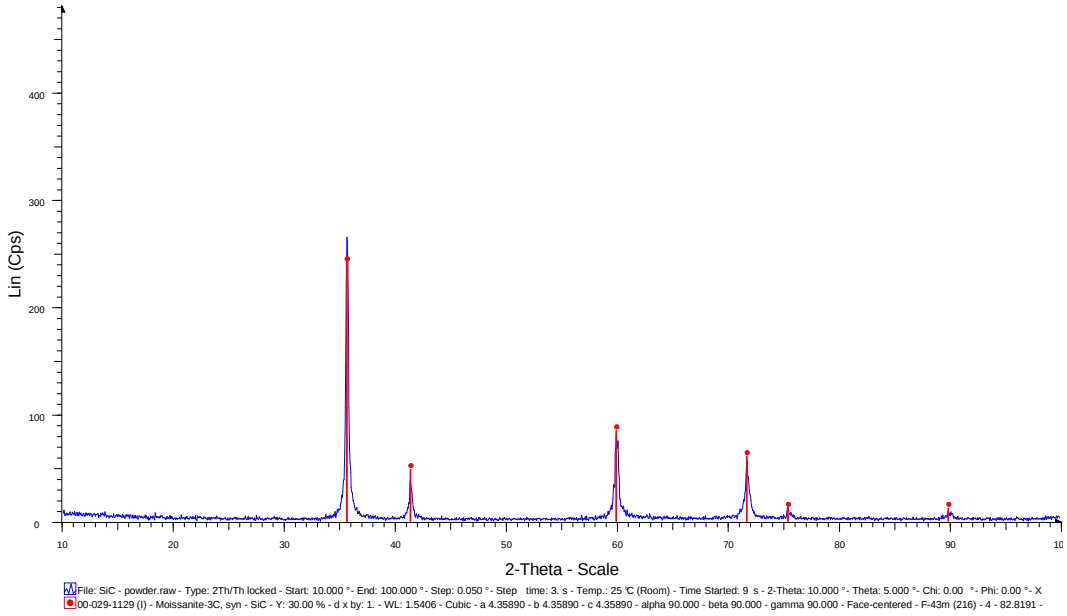

Figure 2-1 XRD analysis of SiC ; in red pattern of SiC, beta

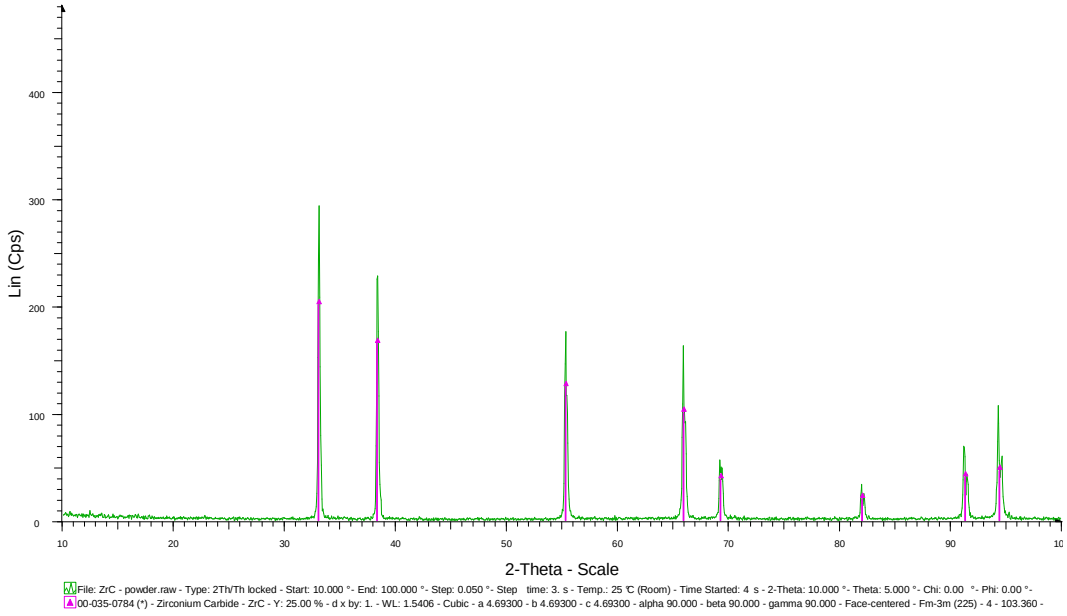

Figure 2-2 XRD analysis of ZrC ; in rose pattern of ZrC

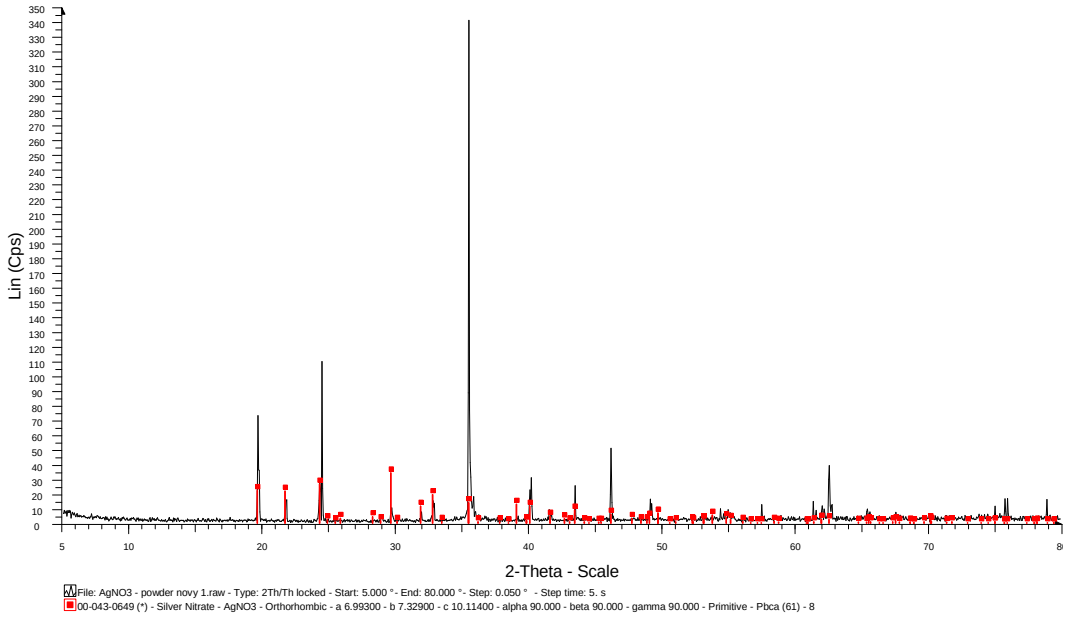

Figure 2-3 XRD analysis of $AgNO_3$, in red pattern of $AgNO_3$

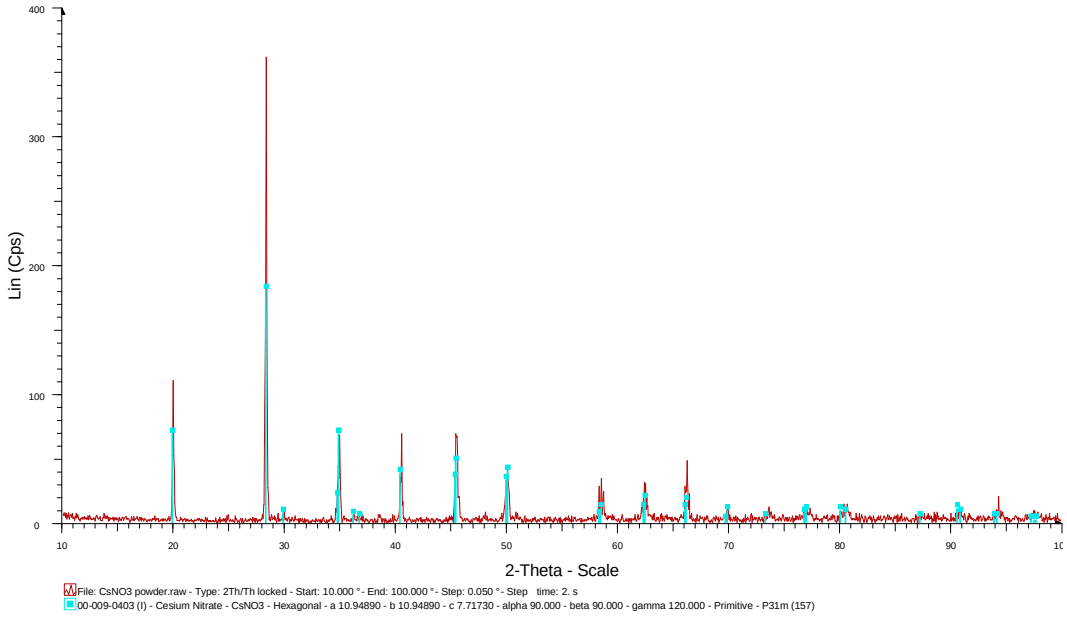

Figure 2-4 XRD analysis of $CsNO_3$, in light blue pattern of $CsNO_3$

2.2. Mixtures preparations

Suitable mixtures of studied carbide and nitrate have been prepared as described in the figure 2-5. A solution of nitrate was drop onto carbide, stirred, ultrasonically treated and vaporization of water took place. Such prepared samples have been again analyzed by XRD.

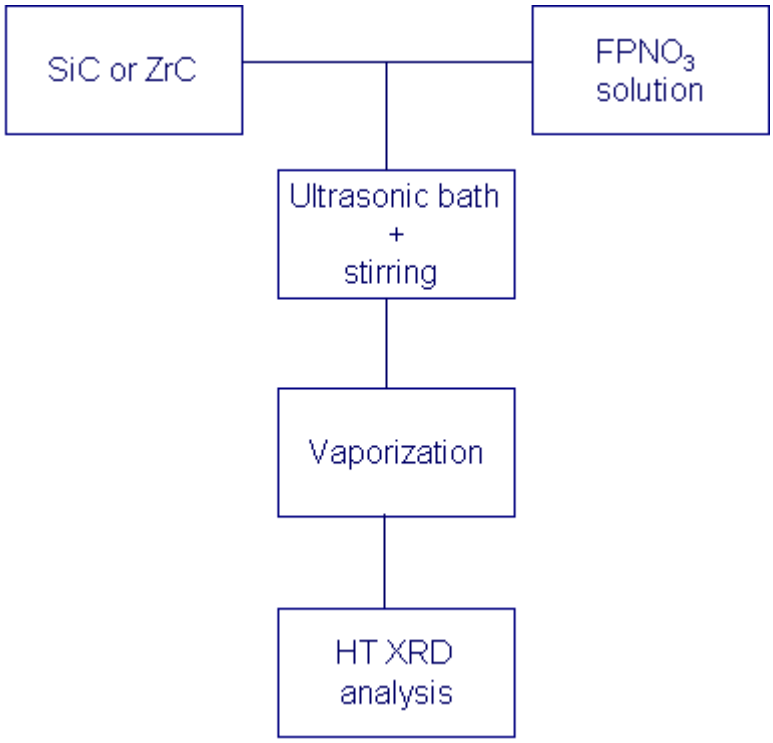

Figure 2-5 Flowchart of the mixture preparation

All prepared mixtures have been measured by XRD to check their right compositions. Figures 2-6 to 2-9 show the prepared mixtures.

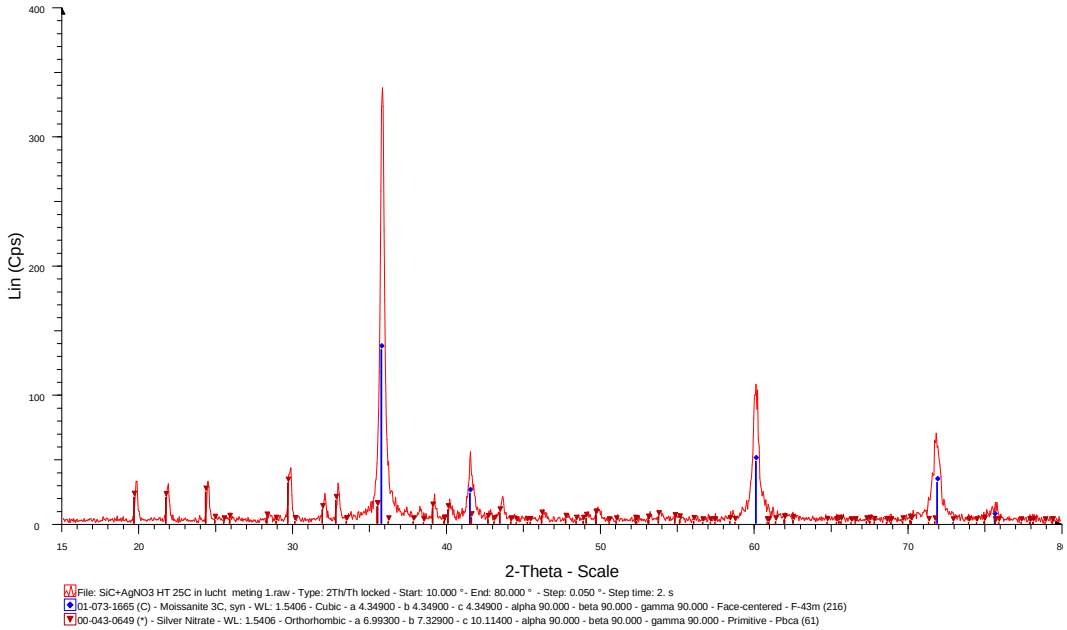

Figure 2-6 XRD measurement of the mixture $SiC+AgNO_3$

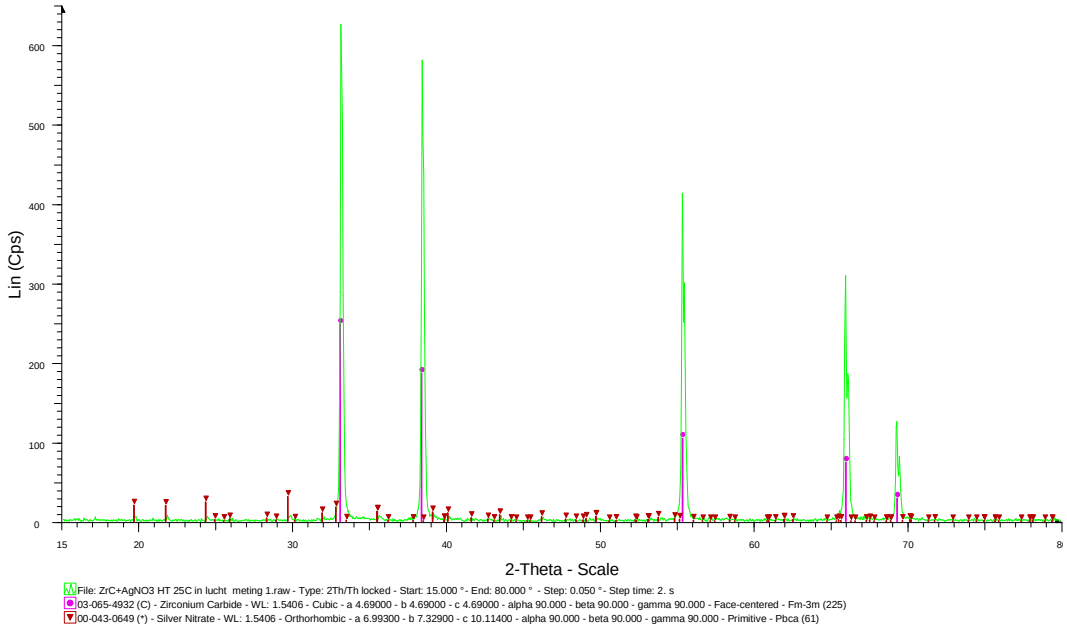

Figure 2-7 XRD measurement of the mixture $ZrC+AgNO_3$

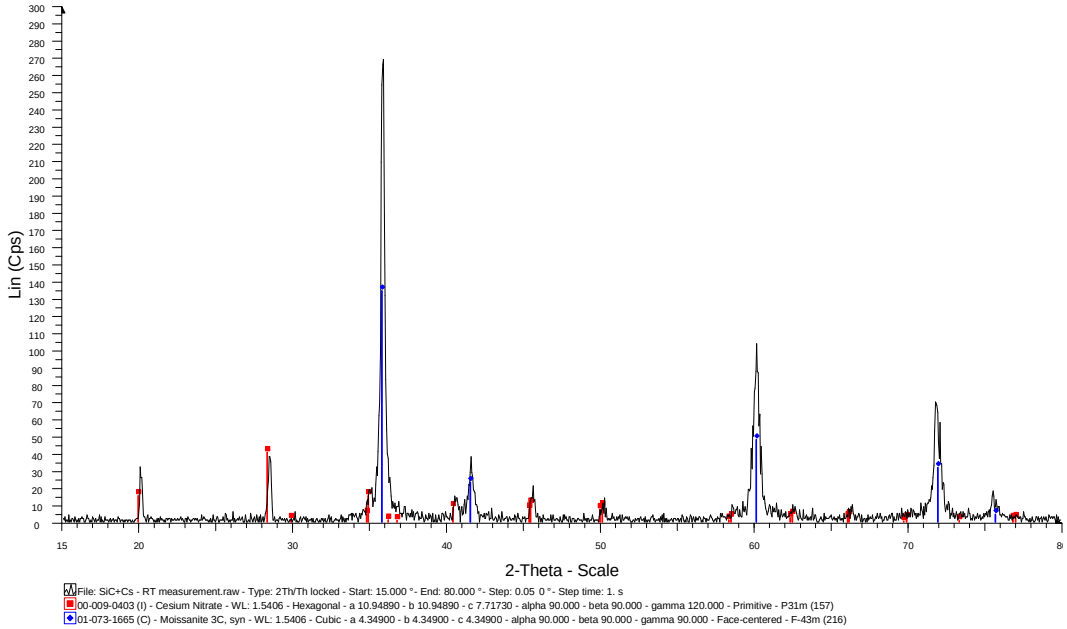

Figure 2-8 XRD measurement of the mixture $SiC+CsNO_3$

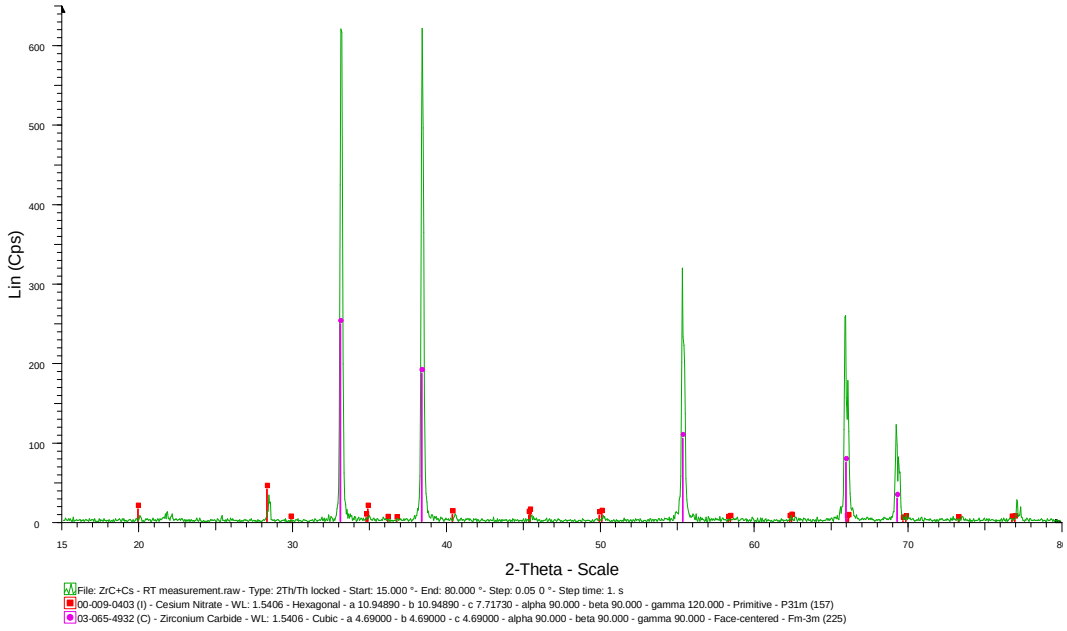

Figure 2-9 XRD measurement of the mixture $ZrC+CsNO_3$

2.3. XRD measurements

All X-ray measurements have been performed by using Bruker AXS D8 ADVANCE X-ray diffractometer for powder diffraction analysis. Measurements have been performed at two different atmospheres – in the air and in the inert atmosphere (N_2). This would give information about influence of the different conditions on the possible occurring reaction.

2.3.1 XRD measurements at room temperature

All performed analyses were realised in the range of 10-100 2Θ, locked coupled, with increment of 0.05, in the air.
These measurements have been realized to check raw materials and the prepared mixtures.

2.3.2 XRD measurements at high temperatures

All HT performed analyses were realised in the range of 10-100 2Θ, locked coupled, with increment of 0.05, in the air or in the inert atmosphere.

The HT XRD analyses to study influence of Ag on the carbides have been done according to the following schedule:

Table 2-1 Temperature schedule for XRD measurements - Ag

Heating rate (ºC/min)	Temperature (ºC)	Time at this temperature (hours)	XRD analyses
-	25	0	yes
2	200	0	no
-	200	1	yes
2	205	0	no
-	205	1	yes
-	205	17	yes
2	250	0	no
-	250	1	yes
2	500	0	no
-	500	1	yes
2	600	0	no
-	600	1	yes
2	700	0	no
-	700	1	yes
2	800	0	no
-	800	1	yes
2	900	0	no
-	900	1	yes
2	1000	0	no
-	1000	1	yes
2	1100	0	no
-	1100	1	yes
2	500	0	no
-	500	1	yes
2	25	0	no
-	25	1	yes

The schedule has been adjusted to the melting temperature of $AgNO_3$ (212 ºC).

The HT XRD analyses to study influence of Cs on the carbides have been done according to the following schedule – this schedule has been adjusted to the melting temperature of $CsNO_3$ (414 ºC).

Table 2-2 Temperature schedule for XRD measurements - Cs

Heating rate (ºC/min)	Temperature (ºC)	Time at this temperature (hours)	XRD analyses
-	25	0	yes
2	200	0	no
-	200	1	yes
2	380	0	no
-	380	1	yes
-	400	17	yes
2	450	0	no
-	450	1	yes
2	500	0	no
-	500	1	yes
2	700	0	no
-	700	1	yes
2	900	0	no
-	900	1	yes
2	1000	0	no
-	1000	1	yes
2	1100	0	no
-	1100	1	yes
2	500	0	no
-	500	1	yes
2	25	0	no
-	25	1	yes

3 Results and discussions – measurements in the air

3.1 SiC with Ag

Mixture has been prepared and HT XRD measurements have been done as mentioned in table 2-1. First, a measurement at room temperature has been done to check the preparation procedure. Figure 3-1 shows that the prepared mixture contains SiC and $AgNO_3$, with a negligible amount of Ag. Between temperatures 100 – 200 ℃, most of the silver nitrate transforms into $AgNO_2$ and Ag. Between temperatures 205 - 205 ℃, $AgNO_3$ disappears and fully transforms into $AgNO_2$ and Ag. After being during 7 hours at the temperature of 205℃, all $AgNO_2$ is fully transformed into silver. There are no changes concerning SiC and no new crystalline phase originating from possible interactions between SiC and Ag.

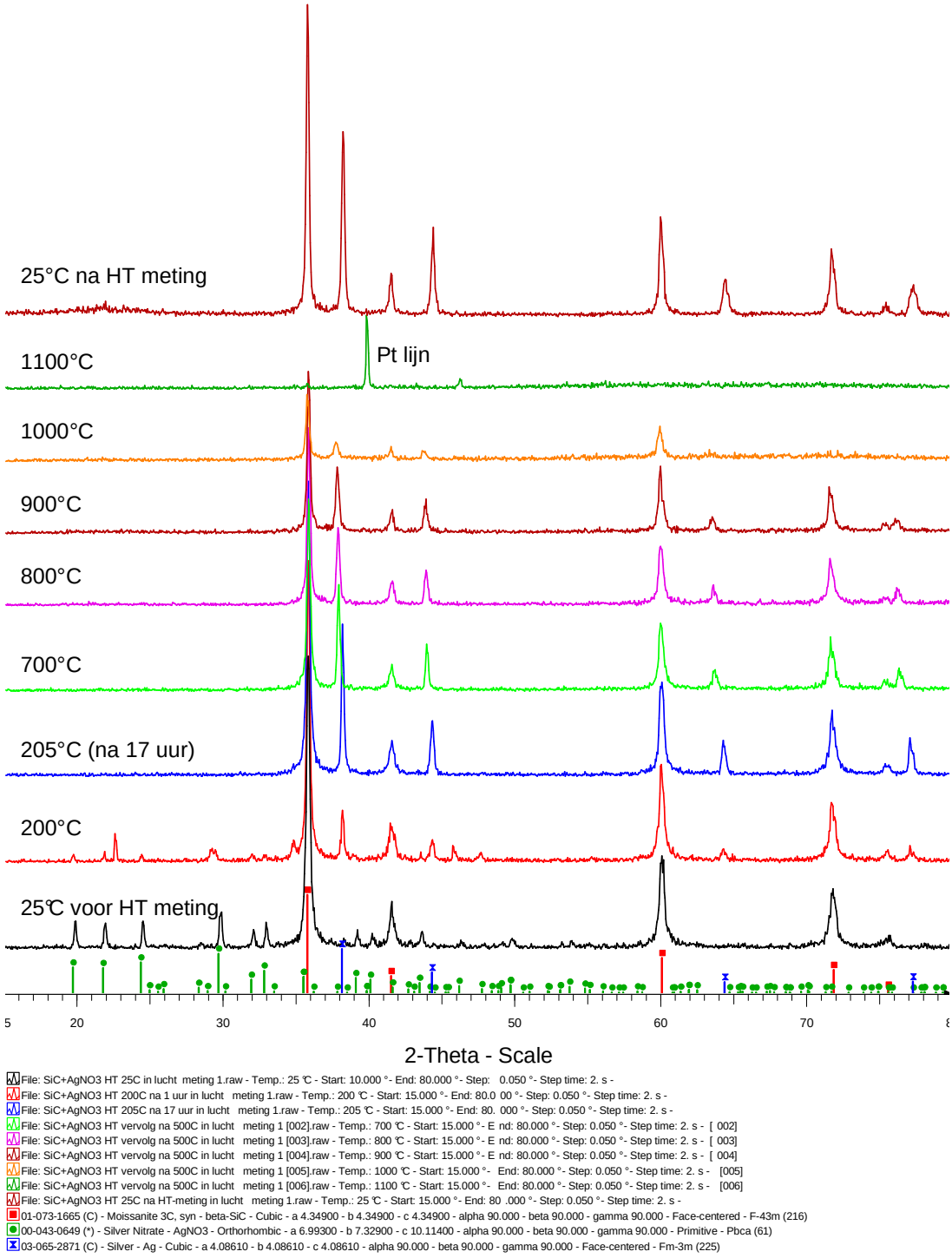

Figure 3-1 HT XRD analysis of SiC + Ag

3.2 ZrC with Ag

The HT XRD analyses have been done as listed in table 2-1.
Silver nitrate is fully transformed into Ag at the temperature of 300 ℃, there are no significant changes at the ZrC structure. At the temperature of about 600 ℃, ZrC begun to oxidise to ZrO_2. At the temperature of about 700 ℃, there is no c rystalline ZrC present anymore, it is fully transformed into ZrO_2. There are no changes concerning silver. No new crystalline phase originating from possible interactions between ZrC and Ag has been detected.

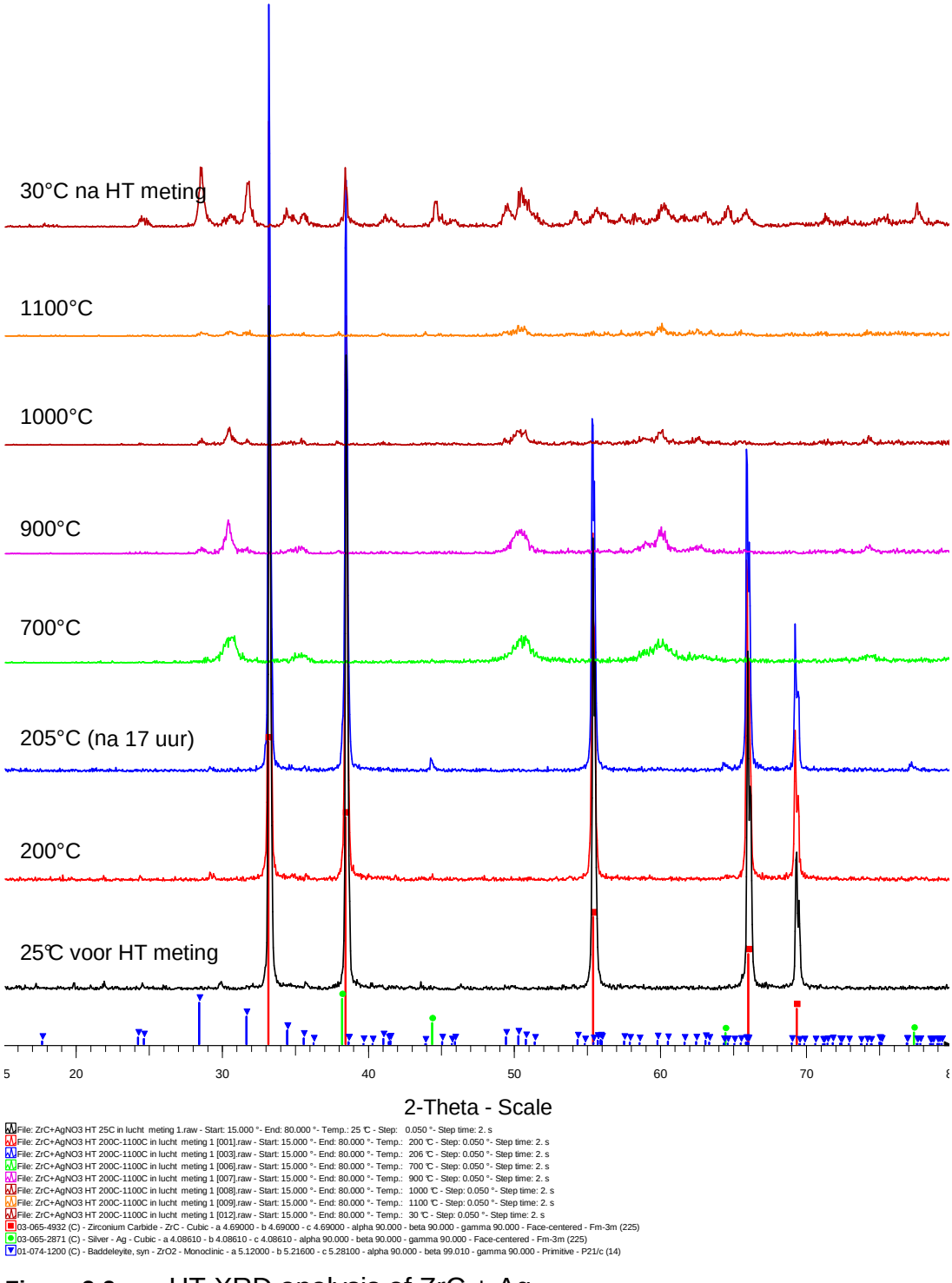

Figure 3-2 HT XRD analysis of ZrC + Ag

3.3 SiC with Cs

Mixture has been prepared and HT XRD measurements have been done as mentioned in table 2-2. First measurement at room temperature has been done to check the preparation procedure. In the following figure, it can be seen that the prepared mixture contains SiC and $CsNO_3$.

During the HT measurement no new phases originated from reaction between SiC and $CsNO_3$ have been found. Around the melting temperature of $CsNO_3$ (400 ºC) and being held at this temperature 17 hours, this compound melts and disappears. At the temperature of 900 ºC first present traces of some new compound appeared. With higher temperatures and during cooling down these peaks became higher and sharper, i.e. the amount of this compound present in the studied system increased. This peak could be identified as a peak of SiO_2, but it is very difficult to identify a compound based only on one peak. This peak does not correspond to any other known compound from the system Si-C-Cs-O-N.

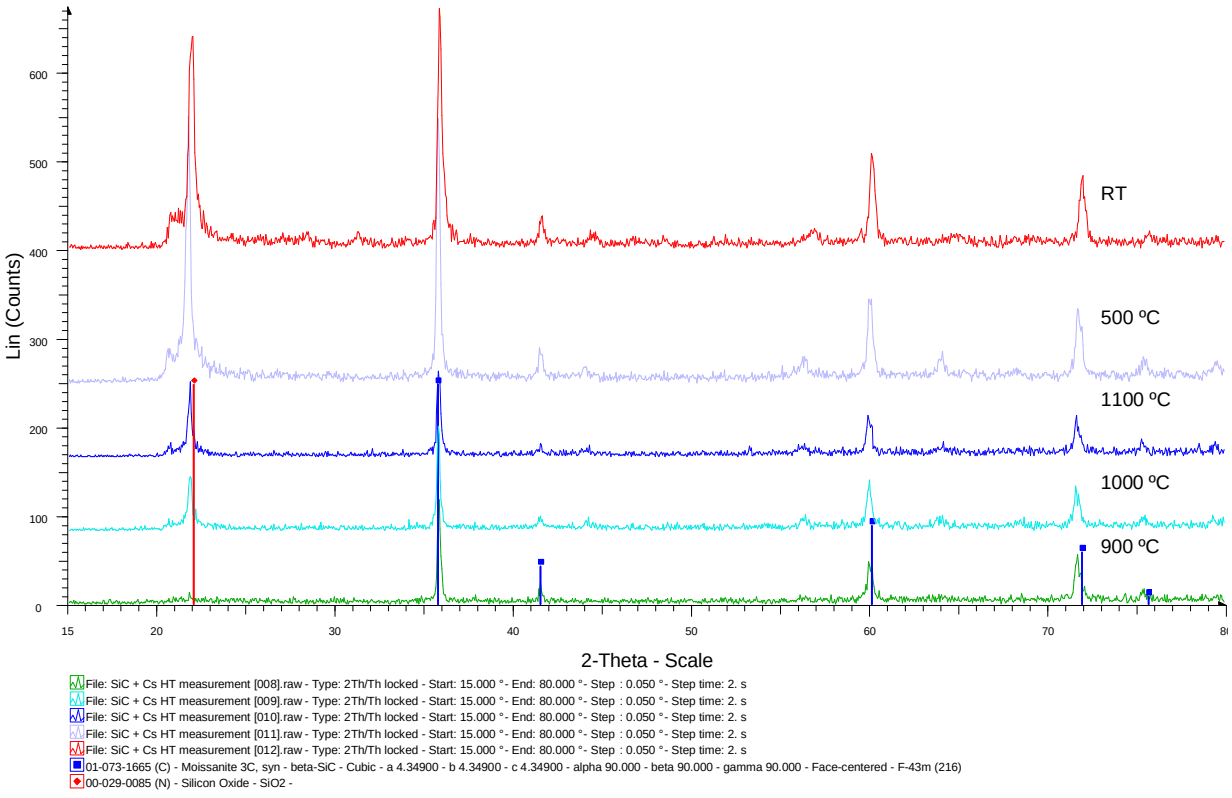

Figure 3-3 HT XRD analysis of SiC + Cs - Detail

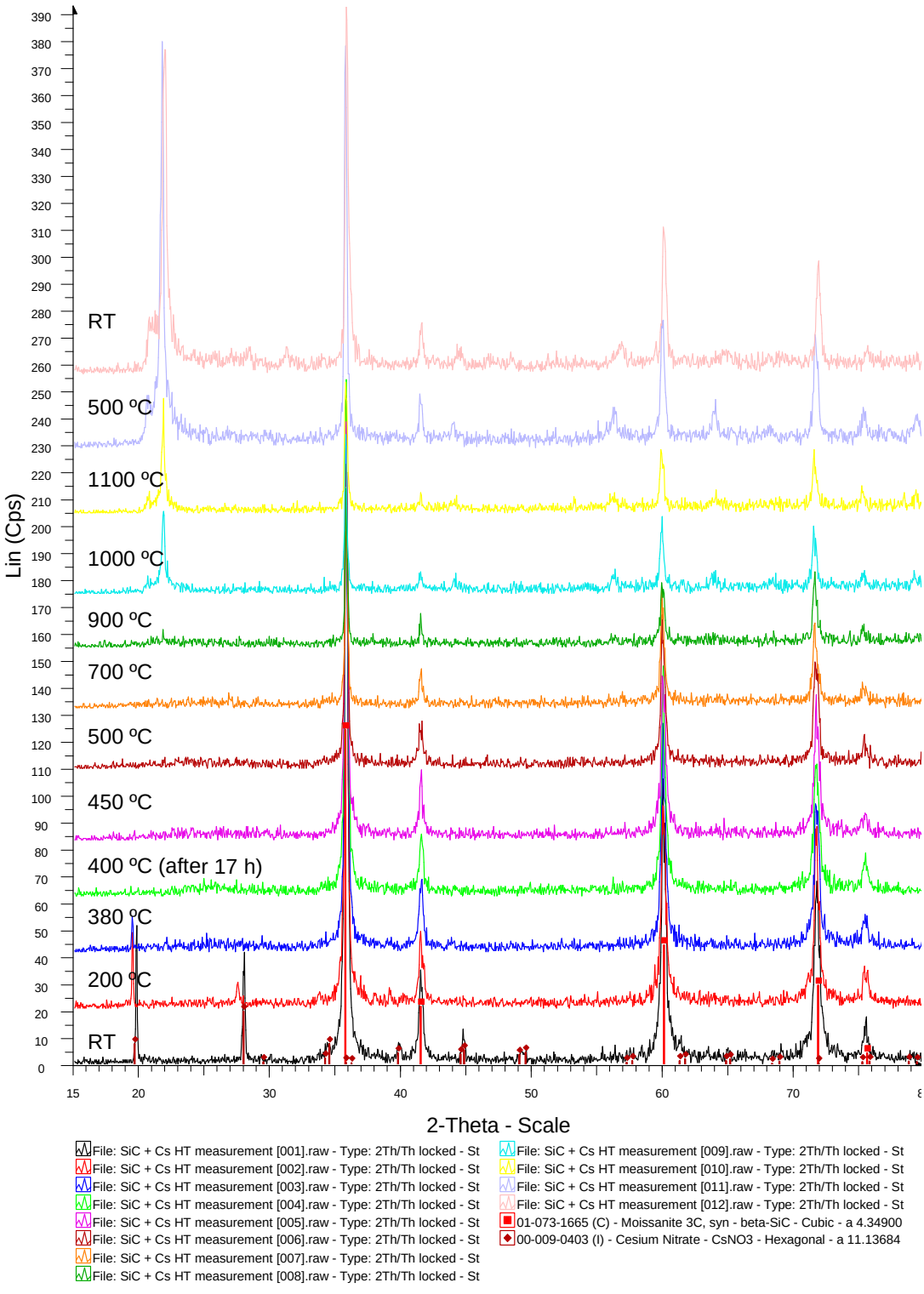

Figure 3-4 HT XRD analysis of SiC + Cs

3.4 ZrC with Cs

Mixture has been prepared and HT XRD measurements have been done as mentioned in table 2-2. First measurement at room temperature has been done to check the preparation procedure. In the following figure, it can be seen that the prepared mixture contains ZrC and $CsNO_3$.

During the HT measurement no new phases originated from reaction between ZrC and $CsNO_3$ have been found. Around the melting temperature of $CsNO_3$ (400 ºC) and being held at this temperature 17 hours this compound melts and disappears. At the temperature of 500 ºC ZrC is fully transformed into ZrO_2 – mixture of different phases (cubic, monoclinic, orthorhombic).

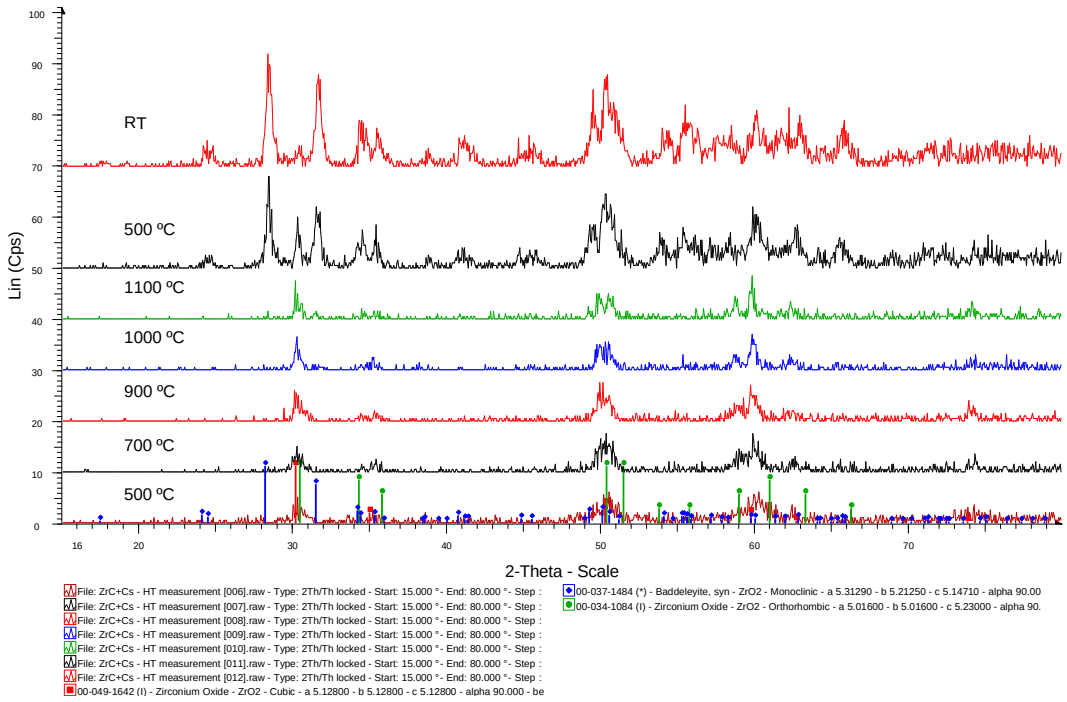

Figure 3-5 HT XRD analysis of ZrC + Cs - Detail

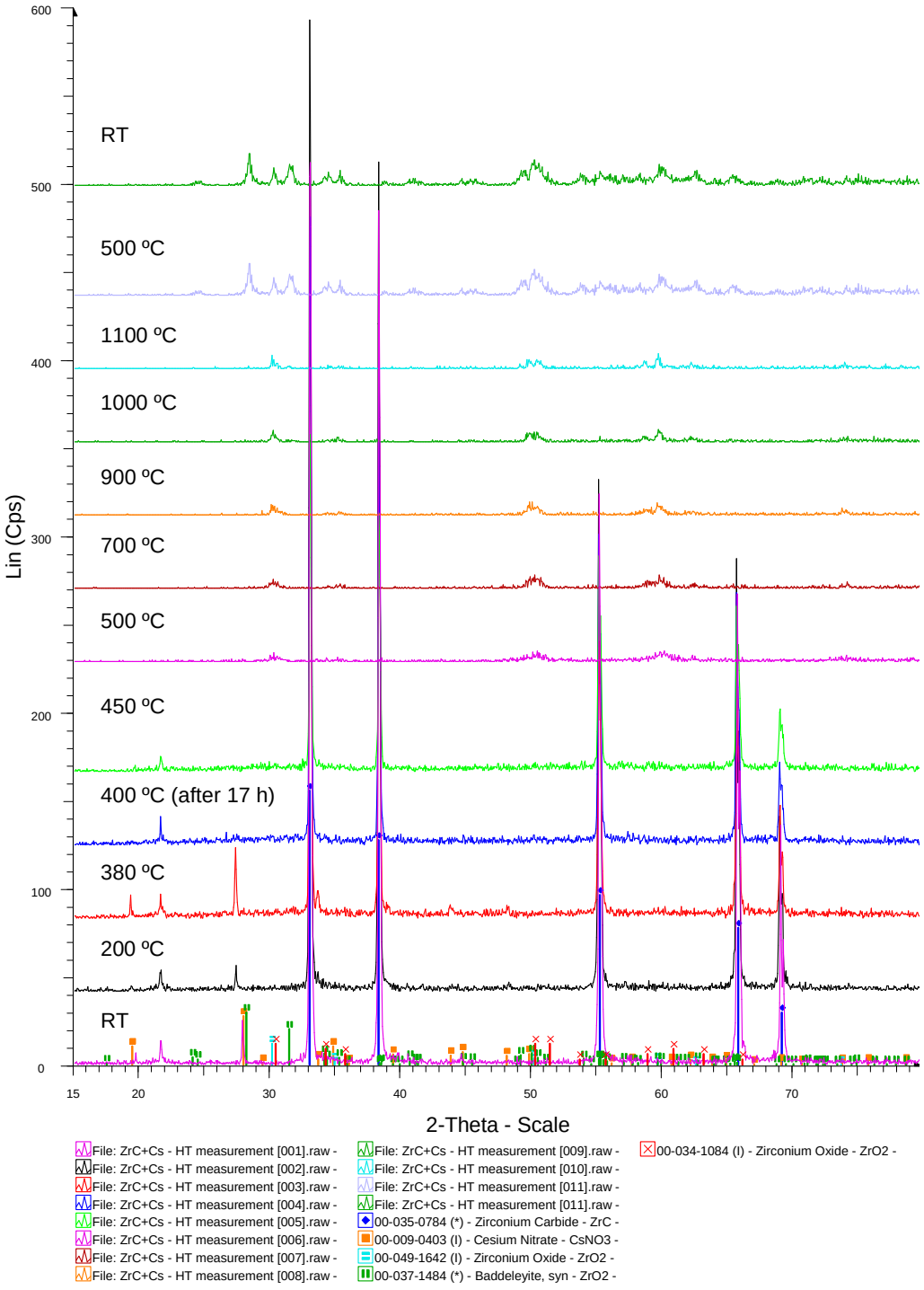

Figure 3-6 HT XRD analysis of ZrC + Cs

4 Results and discussions – measurements in the inert atmospheres

4.1 ZrC with Ag

The HT XRD analyses have been done according to the schedule mentioned in table 2-1, nitrogen served as the inert atmosphere.

Silver nitrate is fully transformed into Ag at the temperature of 300 ℃, there are no significant changes at the ZrC structure. At the temperature of about 600 ℃, ZrC begun to oxidise to ZrO_2. At about 700 ℃, there is no crystalline ZrC anym ore present, it is fully transformed into ZrO_2. There are no changes concerning silver.

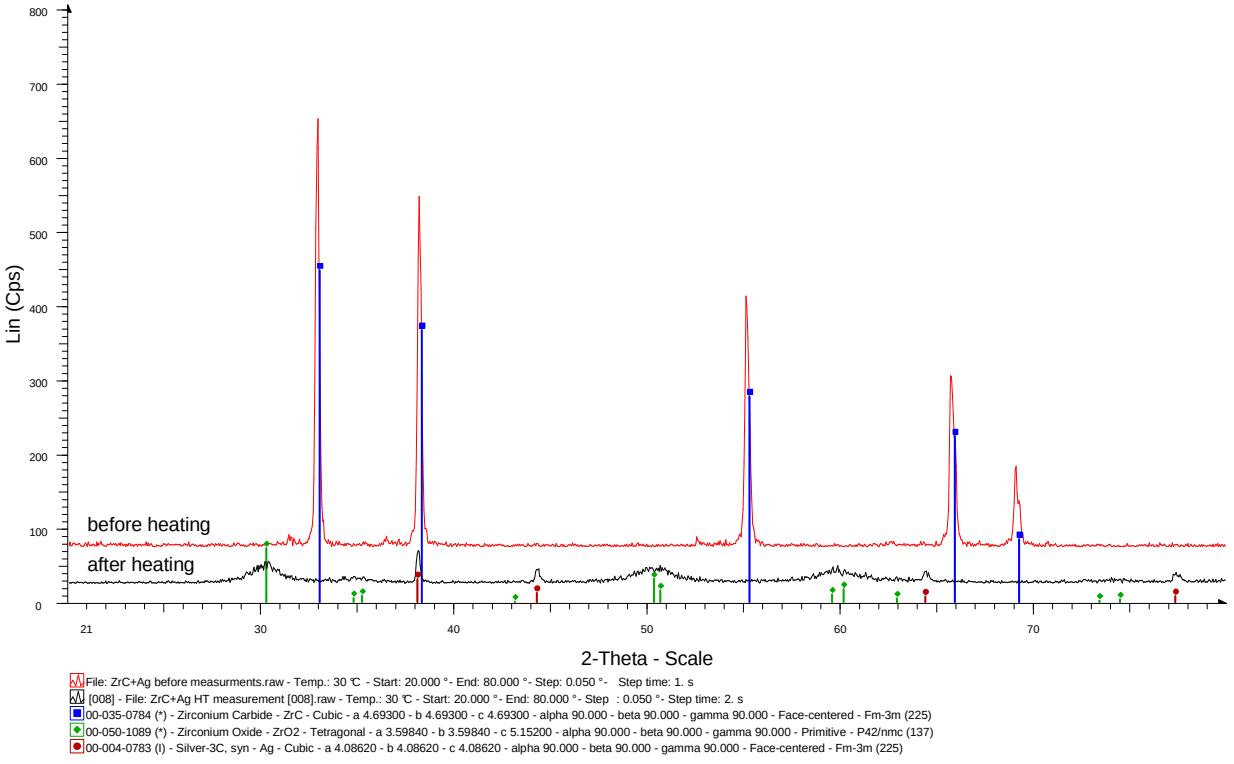

Figure 4-1 HT XRD analysis of ZrC + Ag

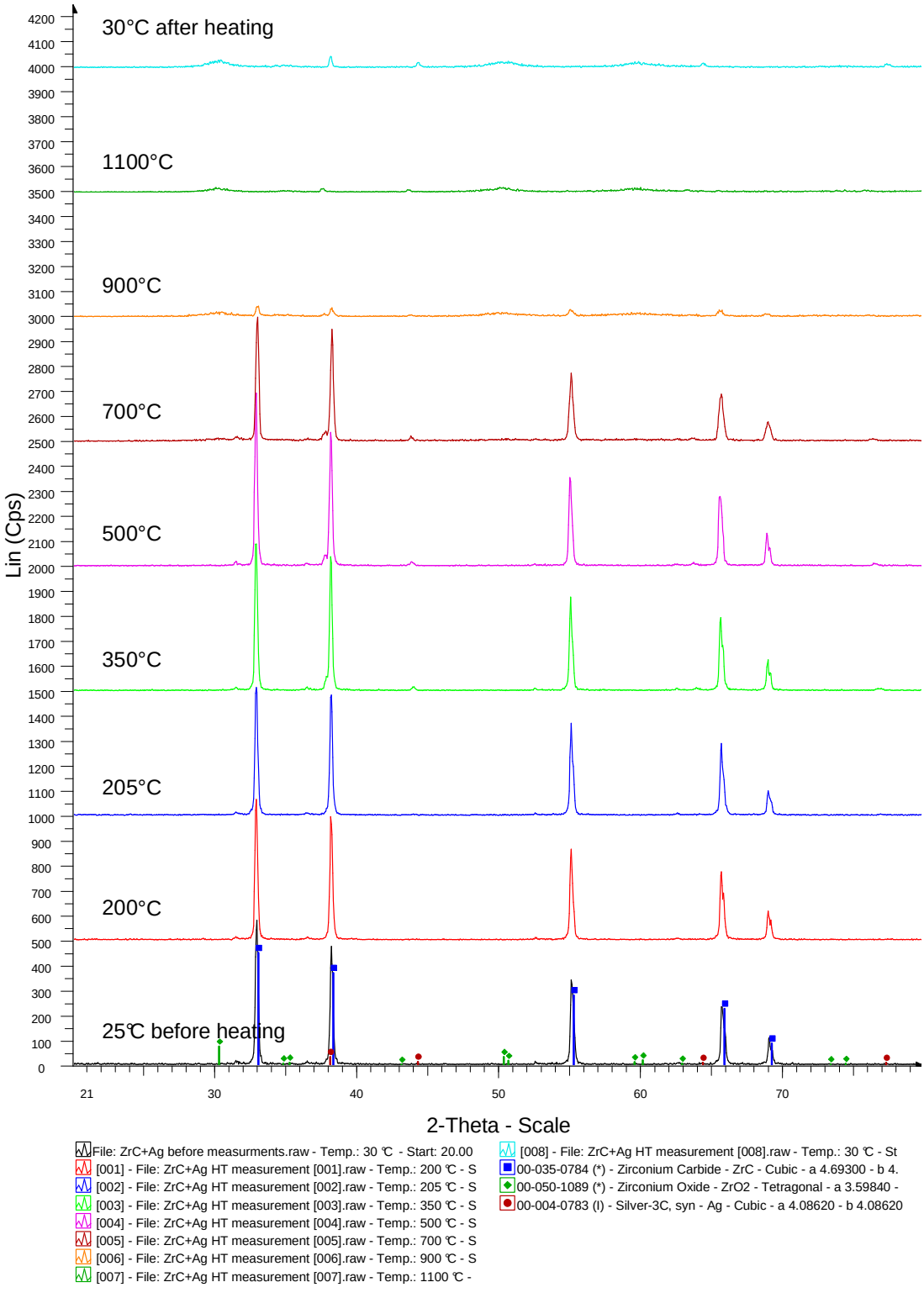

Figure 4-2 HT XRD analysis of ZrC + Ag

4.2 SiC with Cs

Mixture has been prepared and HT XRD measurements have been done as mentioned in table 2-2, nitrogen served as the inert atmosphere.

First measurement at room temperature has been done to check the preparation procedure. In the following figure, it can be seen that the prepared mixture contains SiC and $CsNO_3$.

During the HT measurement no new phases originated from reaction between SiC and $CsNO_3$ have been found. Around the melting temperature of $CsNO_3$ (400 ºC) and being held at this temperature 17 hours this compound melts and disappears. At the temperature of 500 ºC a new peak appeared, this peak could correspond to SiO_2, but as mentioned already above, it is impossible to identify a compound based on one peak only. This peak does not correspond to any other known compound from the system Si-C-Cs-O-N.

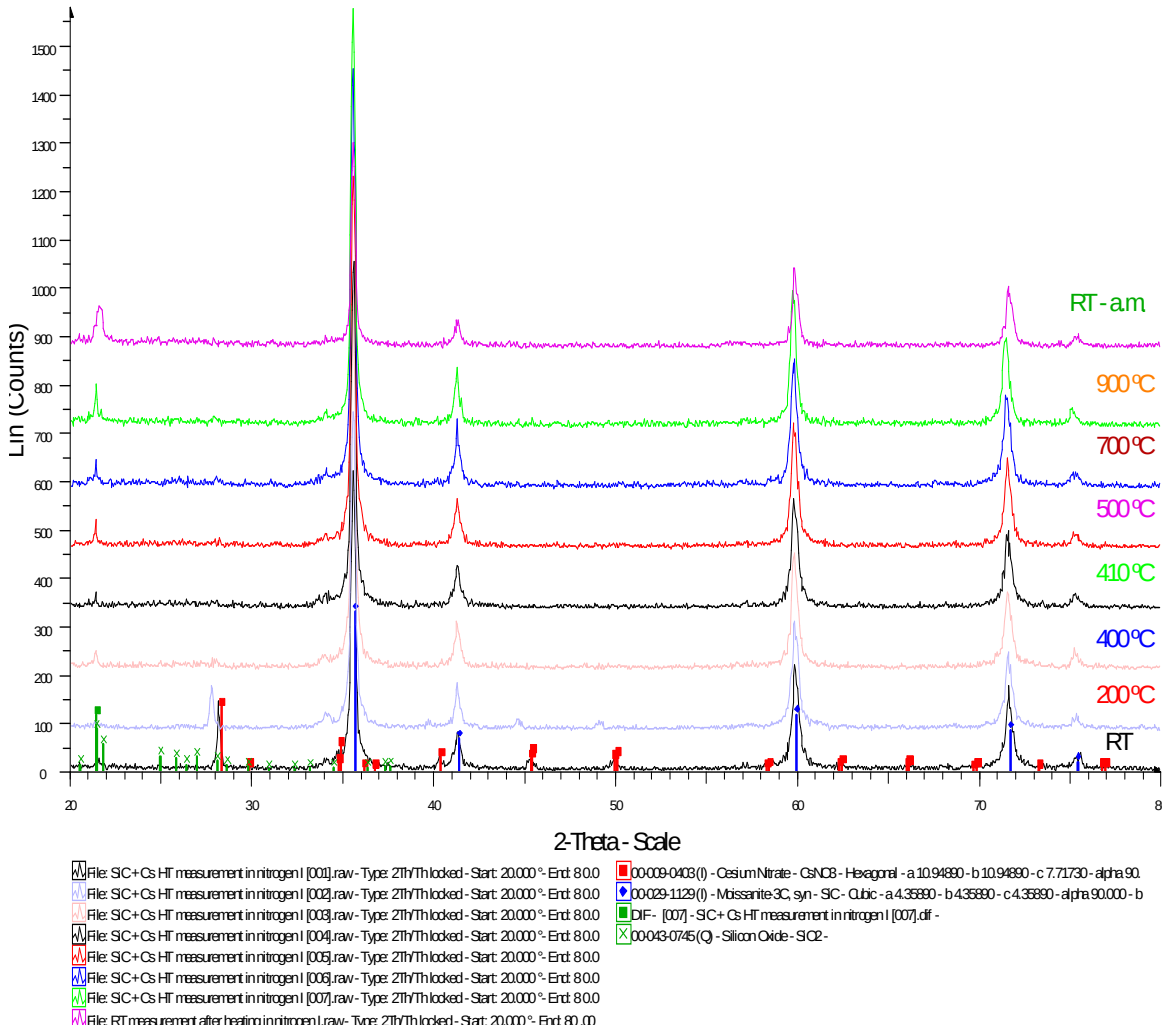

Figure 4-3 HT XRD analysis of SiC + Cs

4.3 ZrC with Cs

Mixture has been prepared and HT XRD measurements have been done as mentioned in table 2-2, nitrogen served as the inert atmosphere.
During the HT measurements no new phases came out from the reaction between ZrC and $CsNO_3$. At the temperature of about 900 ºC ZrC started to oxidize and transformed into ZrO_2, at higher temperatures this transformation is fully completed and no ZrC is present in the studied system.

Figure 4-4 HT XRD analysis of ZrC + Cs - Detail

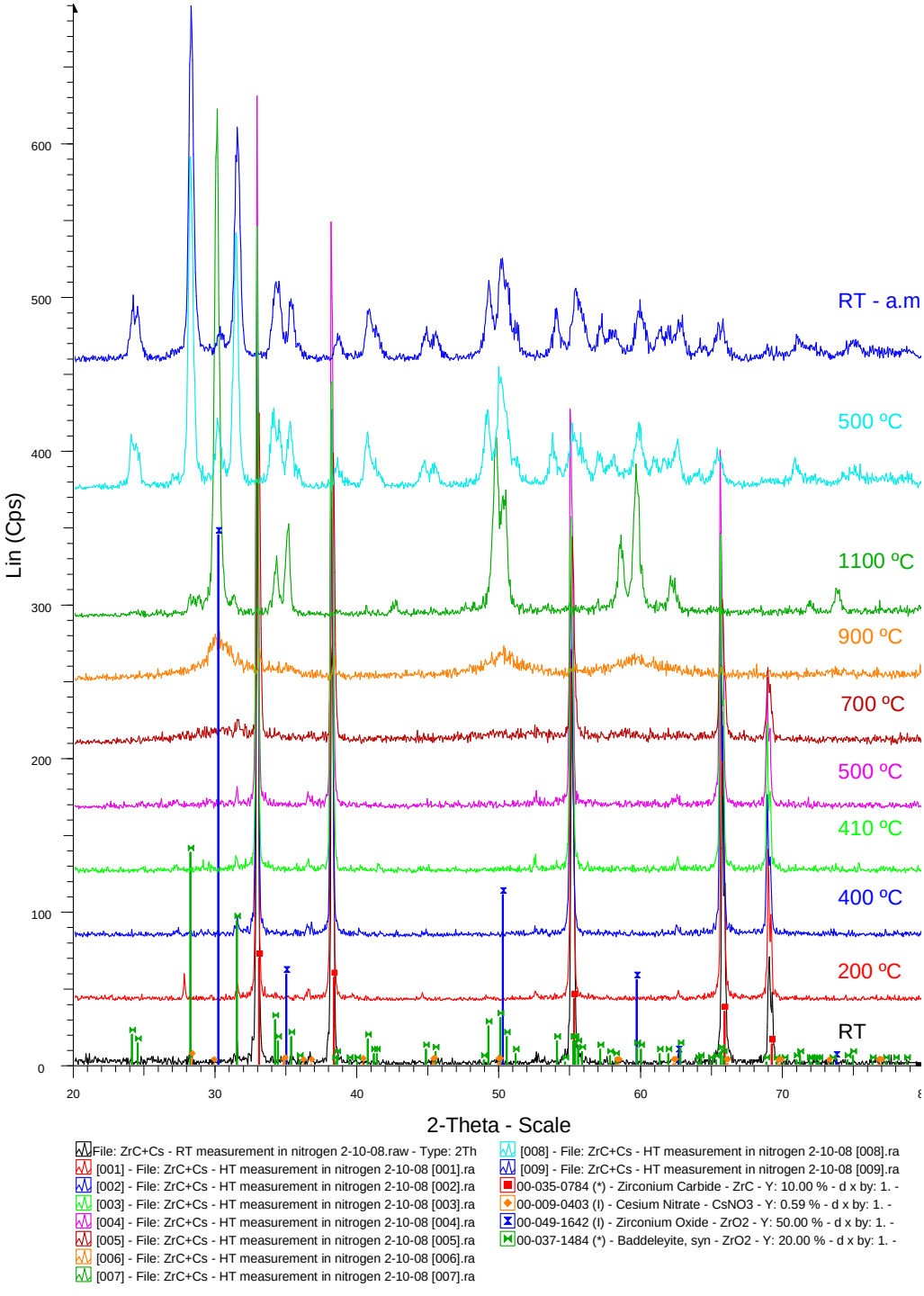

Figure 4-5 HT XRD analysis of ZrC + Cs

5 Conclusions

A study of the interaction between fission products and SiC and ZrC has been performed. Cs and Ag were among the fission products which may well come in contact with carbide layer. The interaction may result in the formation of new phases which may have a negative effect on the stability of the carbide layer.

Mixtures of carbides and suitable Ag/Cs compounds have been prepared. These mixtures have been heated and subsequently checked for their phase composition by X-ray diffraction (XRD). HT XRD has been employed to register possible phase transitions. Measurements have been done in the air and in the inert atmosphere to compare influence of the atmosphere on the behaviour of the studied systems.

No new known crystalline phases (i.e. to be identified by XRD) coming out from the possible interactions between carbides and fission products have been found.

6 Literature

[1] M.J. den Exter (NRG) – Deliverable Raphael D-BF3.2

List of tables

List of figures