

# Crystallization Behaviour of Selected Metal Transition Oxides on Glazes

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**Abstract**— Although the formation of crystals in glazes is well developed, little attention has been apparently paid to the characterization of crystal formation in glazes. As a contribution for and based on compositions used by ceramic artists in the production of crystalline glazes, we studied hereby the effect of zinc, titanium, chromium, cerium, manganese, molybdenum, vanadium, yttrium and zirconium (elements belonging to the transition metals group) in the crystallization of selected glaze matrixes. For that aim selected compositions were milled, homogenized and melted in platinum crucibles. After cooling, the amorphous samples were submitted to a heat treatment at crystallization temperature in order to promote crystallization. The crystalline phases formed during heat treatment were identified by XRD. Results obtained show that the effect of added oxides on crystallization of glazes does not follow a regular behavior even for titanium and zirconium; chromium and molybdenum, which are located in the same group of the periodic table. Zinc and zirconium crystallize in the form of silicates, while titanium and molybdenum crystallize, under certain conditions, as  $\text{CaTiSiO}_5$  and  $\text{CaMoO}_4$  or  $\text{Na}_2\text{Mo}_2\text{O}_7$  respectively. When added individually, chromium, manganese, vanadium and cerium recrystallize the oxide introduced. Iron crystallizes in the form of  $\text{Fe}_3\text{O}_4$ . Yttrium forms  $\text{CaY}_4(\text{SiO}_4)_3\text{O}$  but when combined with vanadium crystallizes in the form of  $\text{YVO}_4$ . In samples where two crystallizing agents were combined, the expected formation of a double silicate between the two components was not observed but titanium and yttrium form with calcium double salts [ $\text{CaTiSiO}_5$  and  $\text{CaY}_4(\text{SiO}_4)_3\text{O}$ ]. Inversion of the amounts of the major and minor components with an effect on crystallization does not lead necessarily to an inversion of crystallizing phases or their amounts.

**Index Terms**— Crystalline glazes, crystallization, nucleation, transition metals, glassy matrix, nucleating agents.

## 1 INTRODUCTION

Crystalline glazes are known since the XIX century and the first experience of its production was a result of an error that developed crystals in a glassy matrix that was expected to be completely amorphous (Creber, 1997; Ahmad et al., 2010). Crystalline glazes attracted initially the attention of ceramic artists, whose interest for crystalline glazes is based on the ornamental effect that the crystals in a glassy matrix confer to a ceramic piece, which is better evaluated in association with the colors, shape and size of developed crystals (Ilsey, 1999).

The little attention that has been apparently paid to the characterization of crystal formation in glazes is surprising since a lot of papers have been published concerning crystallization in glassy and glass-ceramic systems, materials similar to the crystalline glazes (Marotta et al., 1981; Branda et al., 1987; Branda, 1992; Ray and Day, 1993; Koga, 2000)

In these papers the different authors normally use thermal analysis and/or calorimetric methods for identification of the temperatures where transformations occur, while for characterization of the transformations and phases present methods like X-ray diffraction (XRD) complemented by Scanning Electron Microscopy (SEM) and optical microscopy find a wide use. Optical microscopy is particularly used when the amount of crystalline phase may be under the detection limit of the XRD technique, limit that is worsened when a significant amount of an amorphous phase is present (Madivate et al., 1996). The use of Differential Thermal Analysis (DTA) for identification of the regions where transformations occur, seem to have some advantages since this technique is faster and requires smaller amounts of samples (Ray and Day, 1993), contrary to some calorimetric methods.

On the other side calorimetric equipment used for that purpose are normally more sensitive. They show a stable base-

line that allows even the identification of small thermal effects that would be treated as a drift away of the baseline in a DTA diagram (see Figure 1). The equipment used in calorimetry is more expensive and not available in most laboratories, reason why it does not find a wider application in studies like these.

a section that you want to designate with a certain style, the The use of a dynamic technique like DTA in the study of the crystallization of glazes offers advantages in comparison with the methods used in the past, which were based on series of isothermal experiments carried out at different temperatures. Isothermal experiments may not allow identification of all temperatures where transformations occur. On the other side, the dynamic techniques show a major disadvantage due to the fact that some of these transformations occur slowly and do not show a well formed peak, easy to detect and identify.

Crystallization in glass forming systems is frequently attributed to the presence of nucleating agents. Its effect seems to depend, among others, on glaze composition and other factors, reason why there is in the literature no consensual description of the effect of nucleating agents in the crystallization of glassy systems, as one can see from following examples:

- a) Basic components of the glassy matrix show, under favorable conditions, a tendency to crystallize especially in the presence of certain components, which are not necessarily nucleating agents (Booth, 1983). This idea is supported by the results presented by Chang and Jean (1999), Douy and Gervais (2000) and Pernicke et al. (1990), which report the crystallization of some silicates, borates and aluminates from respective matrixes, in the absence of so called nucleating agents;
- b) For some compositions the phases that crystallize from the glassy matrix were the same with or

without nucleating agents (Jordery et al., 1998);

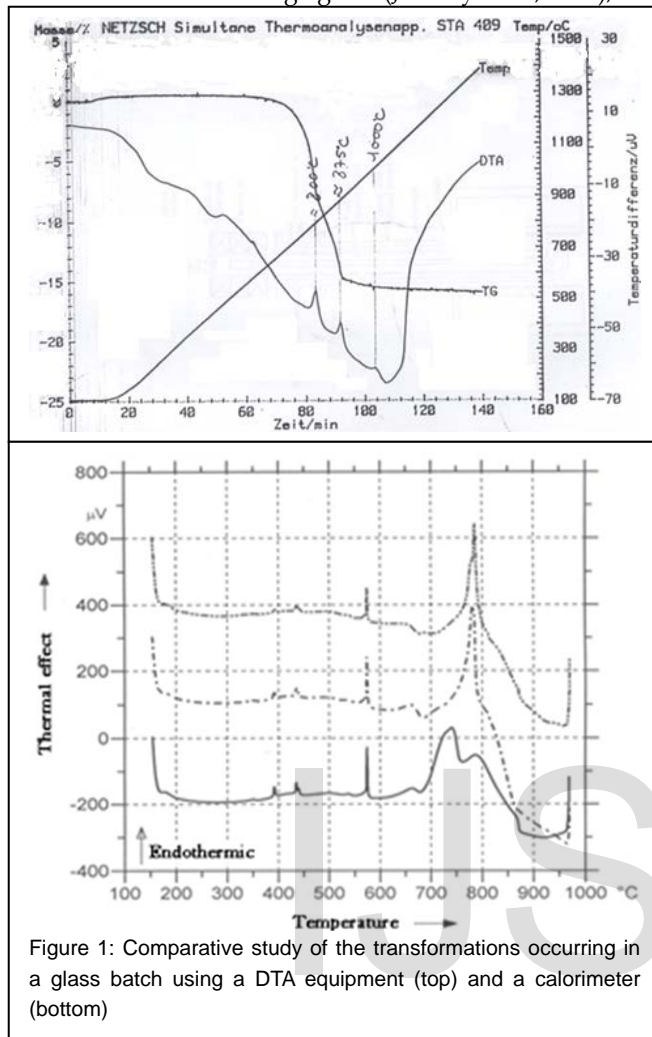


Figure 1: Comparative study of the transformations occurring in a glass batch using a DTA equipment (top) and a calorimeter (bottom)

- c) The effect of the nucleating agent is described in different manners: Pernicke et al. (1990), Jordery et al. (1998) and Shyu and Wang (1996) describe nucleating agents as the components responsible for the reduction or suppression of surface crystallization and promotion of bulk, internal crystallization. It is known that in some systems internal crystallization may become the most relevant form of crystallization, even without addition of nucleating agents;
- d) Vomacka and Wilkinson (1996) treated nucleating agents as components that lower the viscosity of the melt and consequently increasing the kinetics of the crystallization, while Ferrari et.al. (1997) described the effect of a nucleating agent on the increase of crystallization by lowering the activation energy of the process. According to them, addition of nucleating agents may cause crystallization of additional phases.

Based on these results we undertook the present study to understand the crystallization behavior of selected metal transition oxides on glazes. These components were used individual-

ly and in a combination of two (one as the major and the other as the minor component). Amounts of the major and the minor component were inverted to see its influence on crystallizing phases and respective amounts.

## 2 MATERIALS AND METHODS

This study was carried out on samples with compositions obtained from selected references (Booth, 1983; Covert, 1981; Creber, 1997; Dann, 1991; Schimitz, 1984), compositions that were used by pottery ceramists to produce crystalline glazes (see sample compositions in Table 1).

For preparation of samples we used synthetic reagents (AR grade), and for flint we used amorphous silica to facilitate dissolution and formation of the amorphous phase. For the natural raw materials we used the Muiane Kaolin (from Nampula in the North of Mozambique) and the Boane Bentonite (mined in Maputo - Mozambique).

The transition metal oxides used, components responsible for the crystallization of the glazes, were present in the samples alone and as a combination of two components, where one component was present as a major component with contents of approximately 25 - 30% and the second present in small quantities ( $\approx 2 - 6\%$ ). The quantities of the major and minor component were inverted to see the effect of this inversion on the type and amount of the crystallizing phases.

Glaze samples were prepared following a method similar to the one used by Uo et al., 1998 and Baldi et al., 1995: A batch to prepare a glaze with a certain composition was milled and homogenised in a ball mill. After milling, samples were melted in platinum crucibles for about 2 hours in an electric furnace, at approximately 1400°C, and immediately quenched in water.

To achieve a good homogeneity quenched samples were grinded, melted for 30 minutes and quenched again. This cycle was repeated twice.

Melted samples were then submitted to a thermal treatment in an electric furnace at temperatures where crystallization was expected to occur, according to data selected from references were compositions were obtained (Booth, 1983; Covert, 1981; Creber, 1997; Dann, 1991; Schimitz, 1984). At crystallization temperature, soak times of about 3 hours were practiced in order to allow crystals to grow enough to facilitate its characterization by XRD. The dynamic technique was not used in the identification where crystallization occur since results obtained in pre-experiments did not presented evidence of crystallization, due apparently to a low sensitivity of the equipment used.

After cooling, the samples were then milled, the material prepared for XRD analysis using a backloading preparation method. Samples were analyzed with a PANalytical Empyrean Diffractometer with a PIXcel detector and fixed slits with Fe filtered Co- $\alpha$  radiation. Crystallized phases were identified using a PIXcel detector and fixed slits with Fe filtered Co- $\alpha$  radiation and the relative amounts of the phases were estimated using the Rietveld method. Most samples contained an amorphous phase, which has not been included in the quantification.

### 3 RESULTS AND DISCUSSION

Results obtained are presented in Table 1 and 2. These represent the major crystalline phases identified in each sample. Since detection limit of the XRD technique is not good enough, particularly in the presence of glassy phases, minor components may be present, whose identification and quantification was affected by the low detection limit and the presence of the glassy phases.

#### 3.1 Individual Effect of the Oxide on Crystallization

When titanium oxide (TiO<sub>2</sub>) is added (in the form of anatase) the glaze crystallizes rutile and sphene (CaTiSiO<sub>5</sub>), apparently formed by reaction of the oxide with CaO present in Ferro Frit 3110 and SiO<sub>4</sub><sup>2-</sup>. Where Boane bentonite has been added as the clay material XRD analysis showed the presence of hematite (Fe<sub>2</sub>O<sub>3</sub>).

Molybdenum oxide (MoO<sub>3</sub>) crystallizes mainly in two forms: As CaMoO<sub>4</sub> (major crystallizing phase) and Na<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> apparently formed by the reaction of the oxide with CaO and Na<sub>2</sub>O present in Ferro Frit 3110. Small amounts of quartz and cristobalite have been identified. As demonstrated in this document, the numbering for sections upper case Arabic numerals, then upper case Arabic numerals, separated by periods. Initial paragraphs after the section title are not indented. Only the initial, introductory paragraph has a drop cap.

ZnO crystallizes in the form of willemite (Zn<sub>2</sub>SiO<sub>4</sub>) while iron oxide (Fe<sub>2</sub>O<sub>3</sub>) crystallizes magnetite, quartz and cristobalite. Y<sub>2</sub>O<sub>3</sub> leads to the crystallization of CaY<sub>4</sub>(SiO<sub>4</sub>)<sub>3</sub> (main phase) and cristobalite. When ZrO<sub>2</sub> is present as the single crystallizing agent the glaze crystallizes mainly zircon (ZrSiO<sub>4</sub>).

Addition of MnO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, CeO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub>, as individual components, shows no formation of a crystalline phase. Its effect must be better understood since crystallization temperatures used with these oxides were derived from glazes with similar compositions, because of lack of data of glazes using these oxides as crystallizing agents. Introduction of kaolin or bentonite in the composition has no effect on crystallizing phases but seems to alter the amount of crystalline and amorphous phases.

#### 3.2 Effect of Combined Oxides

Table 3 presents the main crystalline phases formed in samples with combination of two different oxides with an expected effect on crystallization of the glaze.

Table 3: Main crystalline phases formed when two crystallizing

agents are combined

Major	Minor	Main crystalline phases formed
ZnO	TiO <sub>2</sub>	Zn <sub>2</sub> SiO <sub>4</sub>
ZnO	ZrO <sub>2</sub>	ZrO <sub>2</sub> and ZrSiO <sub>4</sub>
ZrO <sub>2</sub>	ZnO	ZrSiO <sub>4</sub>
ZrO <sub>2</sub>	TiO <sub>2</sub>	ZrSiO <sub>4</sub>
TiO <sub>2</sub>	ZnO	CaTiSiO <sub>5</sub>
TiO <sub>2</sub>	ZrO <sub>2</sub>	CaTiSiO <sub>5</sub> and ZrSiO <sub>4</sub>
TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	
TiO <sub>2</sub>	MoO <sub>3</sub>	CaMoO <sub>4</sub>
MoO <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	CaMoO <sub>4</sub>
MoO <sub>3</sub>	TiO <sub>2</sub>	CaMoO <sub>4</sub>
Y <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	CaY <sub>4</sub> (SiO <sub>4</sub> ) <sub>3</sub> O

When ZnO (major component) is combined with TiO<sub>2</sub> (minor component) the glaze crystallizes only in the form of Zn<sub>2</sub>SiO<sub>4</sub> (the same phase observed when ZnO is the single crystallizing agent) while, when ZnO (major component) is combined with ZrO<sub>2</sub>, the glaze crystallizes Zn<sub>2</sub>SiO<sub>4</sub> together with zircon (ZrSiO<sub>4</sub>). When zinc appears as minor component no Zn<sub>2</sub>SiO<sub>4</sub> crystallizes.

When ZrO<sub>2</sub> is present as a major component, combined with ZnO or TiO<sub>2</sub>, the glaze crystallizes only in the form of ZrSiO<sub>4</sub>. In samples where ZrO<sub>2</sub> is present as a minor component the glaze crystallizes i) willemite and zircon, when ZrO<sub>2</sub> is combined with ZnO; and ii) a double silicate (CaTiSiO<sub>5</sub>), zircon (ZrSiO<sub>4</sub>); cristobalite and some rutile resulting from transformation of anatase, when ZrO<sub>2</sub> is combined with TiO<sub>2</sub>.

TiO<sub>2</sub> (major component) crystallizes

- i) rutile and a double silicate (CaTiSiO<sub>5</sub>) when combined with ZnO;
- ii) sphene (CaTiSiO<sub>5</sub>), zircon (ZrSiO<sub>4</sub>), cristobalite and rutile when combined with ZrO<sub>2</sub>; and
- iii) calcium molybdate (CaMoO<sub>4</sub>) and rutile when combined with MoO<sub>3</sub>.

MoO<sub>3</sub> (major) forms i) powellite (CaMoO<sub>4</sub>) when combined with Cr<sub>2</sub>O<sub>3</sub> and ii) powellite (CaMoO<sub>4</sub>) and rutile when combined with TiO<sub>2</sub>.

Y<sub>2</sub>O<sub>3</sub> (major) crystallizes CaY<sub>4</sub>(SiO<sub>4</sub>)<sub>3</sub>O and cristobalite when combined with V<sub>2</sub>O<sub>5</sub>. When Y<sub>2</sub>O<sub>3</sub> is present as minor component glaze crystallizes i) powellite (CaMoO<sub>4</sub>) when combined with MoO<sub>3</sub> and ii) wakefieldite (YVO<sub>4</sub>) when combined with V<sub>2</sub>O<sub>5</sub>.

When the amounts of the major and minor oxides are inverted, no inversion of the amounts of phases formed has been necessarily registered:

- a) When ZnO (major) is combined with ZrO<sub>2</sub> (minor) glaze crystallizes Zn<sub>2</sub>SiO<sub>4</sub> and ZrSiO<sub>4</sub>. When ZrO<sub>2</sub> (major) is combined with ZnO (minor) only ZrSiO<sub>4</sub> crystallizes;
- b) When Y<sub>2</sub>O<sub>3</sub> (major) is combined with V<sub>2</sub>O<sub>5</sub> (minor) glaze crystallizes cristobalite and CaY<sub>4</sub>(SiO<sub>4</sub>)<sub>3</sub>O. When V<sub>2</sub>O<sub>5</sub> (major) is combined with Y<sub>2</sub>O<sub>3</sub> (minor) only Wakefieldite crystallizes;
- c) When TiO<sub>2</sub> (major) is combined with ZrO<sub>2</sub> (minor) glaze crystallizes rutile, CaTiSiO<sub>5</sub>, ZrSiO<sub>4</sub> and cristobalite. When ZrO<sub>2</sub> (major) is combined with TiO<sub>2</sub> (minority) only ZrSiO<sub>4</sub> crystallizes.

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### 3.3 Discussion

The analysis of the behaviour of the crystallization of the oxides studied ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{MnO}_2$  and  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ ) shows a great difference in behaviour either when added individually or in a combination of two.

In the samples where  $\text{MnO}_2$  and  $\text{V}_2\text{O}_5$  were added the crystal phase identified represents the form of oxide introduced in sample preparation. In these samples no crystallization of a new phase occurred. Due to the inability to perform dynamic determination of the temperatures where crystallization occurs, it can be assumed that the selected temperature for crystallization does not represent the actual crystallization temperature of these glazes.

Titanium acts as nucleating agent (when present as a minor component) when combined with zinc and zirconium by promoting crystallization of willemite and zircon respectively. But when present as a major component or individually added the glaze crystallizes sphene ( $\text{CaTiSiO}_5$ ) and, additionally, anatase (form of titanium introduced as raw material) is converted to rutile. These results are in agreement with the results obtained by Baldi et al. (1995), De Vekey and Majumdar (1970), Carl et al. (2002) who observed the dual effect of titanium when studying the influence of titanium oxide in the crystallization of glazes. The double salt  $\text{CaTiSiO}_5$  is apparently formed by the reaction of the oxide with the  $\text{CaO}$  present in Frit 3110 and  $\text{SiO}_4^{2-}$ .

Iron oxide crystallizes in the form of magnetite, results in agreement with Dvornichenko and Matsenko (2000) who observed crystallization of magnetite but only when  $\text{Fe}_2\text{O}_3$  content is above 15%.

In samples containing chromium oxide, addition of bentonite and the consequent increase of the iron oxide content, lead to an increase of the amount of  $\text{Cr}_2\text{O}_3$  recrystallizing from the melt, result that is in agreement with the studies of the effect of  $\text{Fe}_2\text{O}_3$  using  $\text{Cr}_2\text{O}_3$  as a nucleating agent in glazes, made by Karamanov et al. (1999) and Rezvani et al. (2005). According to Williamson (1970),  $\text{Cr}_2\text{O}_3$  reduce the growth of crystals by increasing the viscosity, but the addition of small amounts of iron oxide introduced with the bentonite may increase the of crystal growth rate of in the glassy phase. Probably that's why Rezvani (2005) and colleagues report that despite the extensive research conducted to clarify and explain the role of  $\text{Cr}_2\text{O}_3$  as nucleating agent in glazes, there is still a great controversy about the exact role of  $\text{Cr}_2\text{O}_3$  as nucleating agent.

The results obtained for zinc are in agreement with the results obtained by El-Shennawi and Omar (1982), who studied the crystallization of glazes containing zinc with addition of titanium and zirconium oxides. El-Shennawi and Omar (1982) report formation of zinc titanate but no double silicate of zinc with zirconium or zinc with titanium has been registered.

Addition of kaolin and bentonite has apparently an effect on the amount of crystalline phases formed. A comparative analysis of the addition of kaolin and bentonite (Figure 2) in samples with oxides of molybdenum, chromium, cerium and zinc shows an increase the amount of crystalline phases formed. Addition of bentonite also caused an increase of the amount of magnetite (from 35.62% to 62.06%). These results

agree with Williamson (1970), who concludes that small amounts of iron oxide increases the rate of growth of crystals from the glassy phase.

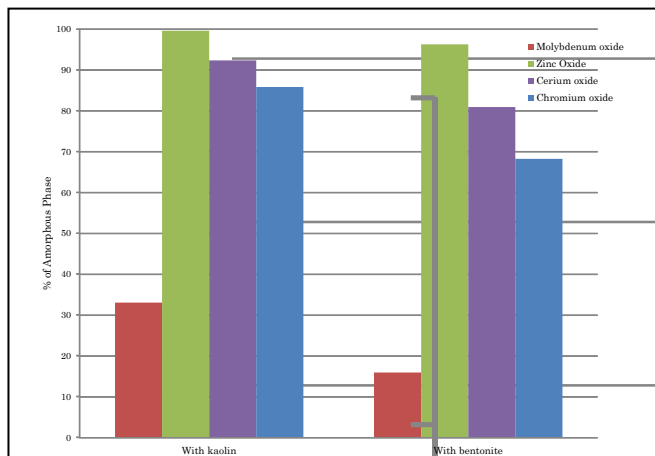


Figure 2: Variation of the amount of amorphous phases with additions of kaolin and bentonite to the glaze matrix

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**Table 1:** Compositions and amounts of crystalline phases in samples with a single crystallizing agent (amorphous phase was not considered in calculations)

#	Amounts of crystalline phases in %	Composition of glazes (amounts in %)				
		Ferro Frit 3110	Flint	Kaolin	Bentonite	Crystallizing agent
AS01	Quartz (4.66), Muscovite ( <b>85.12</b> ) and Ramsdellite (10.22)	57.00	18.00	----	----	<b>MnO<sub>2</sub></b> (25.00)
AS02	Quartz (1.52), Muscovite ( <b>77.74</b> ) and Ramsdellite (20.73)	59.00	15.90	0.50	----	<b>MnO<sub>2</sub></b> (24.60)
AS03	Quartz (4.50), Muscovite ( <b>84.80</b> ) and Ramsdellite (10.70)	49.00	24.50	----	2.00	<b>MnO<sub>2</sub></b> (24.50)
AS04	Rutile (100)	57.00	18.00	----	----	<b>TiO<sub>2</sub></b> (25.00)
AS05	Rutile (100)	59.00	15.90	0.50	----	<b>TiO<sub>2</sub></b> (24.60)
AS06	Rutile ( <b>95.25</b> ) and Hematite (4.75)	49.00	24.50	----	2.00	<b>TiO<sub>2</sub></b> (24.50)
A1	Rutile (45.33) and Titanite (54.67)	46.69	13.54	----	1.40	<b>TiO<sub>2</sub></b> (32.68)
AS07	Molybdate (1.43), Quartz ( <b>53.25</b> ), Powellite (32.03) and Cristobalite (13.29)	57.00	18.00	----	----	<b>MoO<sub>3</sub></b> (25.00)
AS08	Molybdate (1.92), Quartz ( <b>62.28</b> ), Powellite (23.76) e Cristobalite (12.03)	59.00	15.90	0.50	----	<b>MoO<sub>3</sub></b> (24.60)
AS09	Molybdate (3.80), Quartz (14.93), Powellite ( <b>75.35</b> ) and Cristobalite (5.92)	49.00	24.50	----	2.00	<b>MoO<sub>3</sub></b> (24.50)
A2	Molybdate (0.94), Powellite (57.74) and Na <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> (41.32)	57.00	18.00	----	----	<b>MoO<sub>3</sub></b> (25.00)
A3	Molybdate (1.36), Powellite (60.86) and Na <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> (37.78)	59.00	15.90	0.50	----	<b>MoO<sub>3</sub></b> (24.60)
A4	Molybdate (0.60), Powellite (49.91) and Na <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> (49.49)	49.00	24.50	----	2.00	<b>MoO<sub>3</sub></b> (24.50)
AS10	Cerianite (100)	57.00	18.00	----	----	<b>CeO<sub>2</sub></b> (25.00)
AS11	Cerianite (100)	59.00	15.90	0.50	----	<b>CeO<sub>2</sub></b> (24.60)
AS12	Cerianite ( <b>65.59</b> ) and Apatite [Sr-bearing] (36.41)	49.00	24.50	----	2.00	<b>CeO<sub>2</sub></b> (24.50)
AS13	Willemite (100)	57.00	18.00	----	----	<b>ZnO</b> (25.00)
AS14	Willemite (100)	59.00	15.90	0.50	----	<b>ZnO</b> (24.60)
AS15	Willemite (100)	49.00	24.50	----	2.00	<b>ZnO</b> (24.50)
AS16	Eskolaite (100)	57.00	18.00	----	----	<b>Cr<sub>2</sub>O<sub>3</sub></b> (25.00)
AS17	Eskolaite (100)	59.00	15.90	0.50	----	<b>Cr<sub>2</sub>O<sub>3</sub></b> (24.60)

AS18	Eskolaite (100)	49.00	24.50	----	2.00	<b>Cr<sub>2</sub>O<sub>3</sub></b> (24.50)
AS19	Hematite ( <b>59.08</b> ), Magnetite (35.62), Cristobalite (2.79) and Quartz (2.50)	57.00	18.00	----	----	<b>Fe<sub>2</sub>O<sub>3</sub></b> (25.00)
AS20	Hematite ( <b>56.69</b> ), Magnetite (35.06), Cristobalite (4.44) and Quartz (3.81)	59.00	15.90	0.50	----	<b>Fe<sub>2</sub>O<sub>3</sub></b> (24.60)
AS21	Hematite (36.60), Magnetite ( <b>62.06</b> ), Cristobalite (0.70) and Quartz (0.64)	49.00	24.50	----	2.00	<b>Fe<sub>2</sub>O<sub>3</sub></b> (24.50)
AS22	Yttrium Oxide (2.39), Cristobalite (6.58) and CaY <sub>4</sub> (SiO <sub>4</sub> ) <sub>3</sub> O ( <b>91.03</b> )	47.14	18.02	0.60	----	<b>Y<sub>2</sub>O<sub>3</sub></b> (30.15)
AS23	Yttrium Oxide (5.22) and CaY <sub>4</sub> (SiO <sub>4</sub> ) <sub>3</sub> O ( <b>94.78</b> )	47.14	18.02	0.60	----	<b>Y<sub>2</sub>O<sub>3</sub></b> (8.18)
AS24	Scherbinaite (100)	47.14	18.02	0.60	----	<b>V<sub>2</sub>O<sub>5</sub></b> (8.18)
AS25	Scherbinaite (100)	47.14	18.02	0.60	----	<b>V<sub>2</sub>O<sub>5</sub></b> (30.15)
A5	Willemite (78.24) and Zircon (21.76)	49.00	24.50	----	2.00	<b>ZrO<sub>2</sub></b> (24.50)
A6	Baddeleyite (36.54) and Zircon (63.46)	46.69	13.54	----	1.40	<b>ZrO<sub>2</sub></b> (32.68)

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**Table 2:** Amounts of crystalline phases in samples where two crystallizing agents were combined (amorphous phase was not considered in calculations)

Sample	Amounts of crystalline phases in %	Amounts of crystallizing agents in %						
		MoO <sub>3</sub>	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	ZnO	ZrO <sub>2</sub>
AS26	TiO <sub>2</sub> (83.79) and CaMoO <sub>4</sub> (16.21)	5.86	28.38	----	----	----	----	----
AS27	CaMoO <sub>4</sub> (65.37) and Cr <sub>2</sub> O <sub>3</sub> (34.63)	28.38	----	5.86	----	----	----	----
AS28	CaMoO <sub>4</sub> (100)	28.38	----	----	5.86	----	----	----
AS29	V <sub>2</sub> O <sub>5</sub> (100)	5.86	----	----	----	28.38	----	----
AS30	Cr <sub>2</sub> O <sub>3</sub> (96.47) and TiO <sub>2</sub> (3.53)	----	5.86	28.38	----	----	----	----
AS31	TiO <sub>2</sub> (100)	----	28.38	----	----	5.86	----	----
AS32	Cr <sub>2</sub> O <sub>3</sub> (100)	----	----	28.38	----	5.86	----	----
AS33	Y <sub>2</sub> O <sub>3</sub> (2.69), SiO <sub>2</sub> (11.92) and CaY <sub>4</sub> (SiO <sub>4</sub> ) <sub>3</sub> O (85.39)	----	----	----	28.38	5.86	----	----
AS34	YVO <sub>4</sub> (100)	----	----	----	5.86	28.38	----	----
A7	Zn <sub>2</sub> SiO <sub>4</sub> (100)	----	5.86	----	----	----	28.38	----
A8	TiO <sub>2</sub> (58.66) and CaTiSiO <sub>5</sub> (41.34)	----	28.38	----	----	----	5.86	----
A9	ZrO <sub>2</sub> (8.42) and ZrSiO <sub>4</sub> (91.58)	----	----	----	----	----	5.86	28.38
A10	Zn <sub>2</sub> SiO <sub>4</sub> (76.58) and ZrSiO <sub>4</sub> (23.42)	----	----	----	----	----	28.38	5.86
A11	TiO <sub>2</sub> (59.44), CaTiSiO <sub>5</sub> (33.95), ZrSiO <sub>4</sub> (5.70) and SiO <sub>2</sub> (0.90)	----	25.66	----	----	----	----	2.94
A12	ZrO <sub>2</sub> (12.23) and ZrSiO <sub>4</sub> (87.77)	----	2.94	----	----	----	----	25.66



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