

***In-situ* Clinkerization Study of Belite Portland Clinkers by Synchrotron X-ray Powder Diffraction**

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1. Introduction.

The production of one ton of standard Portland cement releases into the atmosphere 0.54 tons of CO₂ resulting from the decomposition of calcite. Moreover, the manufacturing processes need high amounts of energy, mainly for clinkering and milling. Thus, taking into account calcite decarbonation and burning of the fuel in the kilns and the electricity consumption to obtain a ton of cement, 0.97 tons of CO₂ are released into atmosphere. This implies that the overall CO₂ emissions from the cement industry are ~ 6% of all anthropogenic carbon dioxide and account for 4% of the global warming of the planet [1]. Finding effective ways for reducing such emissions is therefore a strong research priority. Belite Portland (BP) clinkers may be an environmentally-friendly alternative as their production process leads to lower CO₂ emissions than that of ordinary Portland cements, OPCs.

BP clinkers contain more than 50 wt% of belite, Ca₂SiO₄ (C₂S) as the main crystalline phase, while OPC main phase is alite, Ca₃SiO₅ (C₃S). This difference leads a decrease in calcite demand and consequently a reduction of 0.04 tons of CO₂ per ton of BP clinker produced from the decomposition of calcite [2]. Moreover, the formation of the principal component of BP clinkers, belite, requires the use of a clinkerization temperature of about 1350°C in the kiln, 100°C lower than that for standard Portland clinker [3,4] which helps to reduce CO₂ emissions from fuel burning. It must also be underlined that lower burning temperatures may lead to phases with lower microparticle sizes which should hydrate faster as they have higher surface-to-volume ratios (for a given Blaine milling).

BP cements-based concretes are considered to be “low heat” ones and they are more durable than those derived from OPCs. These performances make BP cements suitable for the construction of large dams and for the lining of oil wells. However, the massive application of these materials requires overcoming two main drawbacks: i) the low hydration rate of the belite phase, which leads to develop of low strengths at early hydration ages; and ii) the high hardness in the cement-milling process [5,6].

Stoichiometric C_2S presents five polymorphs on heating, γ , β , α'_L , α'_H and α . One kind of activation of BP clinkers consists on the stabilisation at room temperature of the high temperature polymorphs (i.e. α forms), which are more reactive than β - C_2S [7]. The latter is the polymorph that commonly prevails in OPCs but due to its slow hydration kinetic they develop very little mechanical strength at early ages. The activation may be carried out by conventional firing using minor elements (dopants-activators) such as alkalis, sulphur or barium additions [8] or by specific thermal treatments [9,10].

The main aim of this work is to better understand the clinkerization process of BP clinkers. The clinkerization of standard Portland clinkers has been extensively investigated over the years [11]. Reactions/transformations at high temperature and the influence of minor elements in BP clinkers formation have to be established, as they may improve final cement performances. Clinkerization is considered to be a very complex process as it comprises solid state reactions, liquid phase appearance, polymorphic transformations on heating, and polymorphic stabilisation and crystallisation on cooling. Main reactions/processes occur at very high temperature, up to 1200°C. This set of behaviours makes the study of the process a difficult task. The use of ultra-high resolution synchrotron X-ray powder diffraction, SXRPD, is highly desirable for studying such complex reactions. As the X-rays may be highly energetic, the absorption is minimized, which allows the use of Pt capillaries to perform very high temperature *in-situ* studies [12]. Moreover, the used of transmission geometry (rotating capillary) leads to the illumination of the full sample avoiding poor particle statistics. On the other hand it is of great importance to obtain high resolved data in order to help to minimize the problem of strong peak overlapping in the patterns [13].

2. Experimental section.

2.1. Samples preparation.

In order to prepare belite clinkers, the initial raw mixtures were done by mixing appropriated amounts of calcite (99% Aldrich), kaolin (Aldrich), quartz (99.59% ABCR) and iron oxide (99.95% Alfa Aesar). To promote activation K_2CO_3 (99% Aldrich) and/or Na_2CO_3 (99.999% Aldrich) were added. Table 1 gives the dosages, as oxides, used to prepare the studied laboratory clinkers. The raw mixtures were prepared in order to obtain clinkers with the following theoretical phase composition: 60 wt% of C_2S , 16 wt% of C_3S , 8 wt% of C_3A , 16 wt% of C_4AF . Other compositions were also studied, including samples with Na_2O and SO_3 added as activators. The results for these samples will be reported elsewhere.

Table 1. Dosages used to obtain the studied three clinkers, expressed as oxide in weigh percent. The amount of activator added is highlighted in bold.

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	MgO	SrO
B_ref	62.84	25.00	6.34	5.23	0.27	0.13	0.07	0.09
B_1.0K	62.38	24.81	6.29	5.19	1.01	0.13	0.07	0.09
B_0.5NK	62.43	24.85	6.30	5.20	0.50	0.50	0.07	0.09

Raw materials were mixed by hand in an agate mortar with the aid of ethyl alcohol and dried in a stove at 60 C. This treatment was performed by triplicate. Then, the raw mixtures were openly heated at 1000°C for 1 hour in Pt crucibles, in order to achieve decarbonation. These preheated (decarbonated) mixtures were introduced into the Pt capillaries in the laboratory. These capillaries have an external diameter of 0.6 mm and a wall size of 40 µm. The folded filled capillaries were ready for the *in-situ* synchrotron study.

2.2. High temperature synchrotron X-ray powder diffraction data acquisition and analysis.

Synchrotron X-ray powder diffraction (SXRPD) patterns have been collected on ID31 diffractometer in Debye-Scherrer (transmission) configuration of ESRF, European Synchrotron Radiation Facility, (Grenoble, France) using a wavelength $\lambda=0.300715(9)$ Å (41.22 keV) selected with a double-crystal Si (111) monochromator and calibrated with Si NIST ($a=5.431195$ Å). The Pt capillaries were rotated during data collection. The data acquisition time was ≈ 45 min at each temperature to have very good statistics over the angular range 1.0-20° (in 2 θ). The data from the multi-analyser Si(111) stage coupled with seven scintillation detectors were normalised and summed up to 0.003° step size with local software to produce the final raw data.

A parabolic mirror furnace was used to heat the samples between 1000°C and 1400°C [12].

X-ray powder diffraction patterns were analysed by using the Rietveld method as implemented in the GSAS software package [14]. Peak shapes were fitted by using the *pseudo-Voigt* function [15] with the axial divergence correction implemented [16]. The regions were the Pt peaks gave significant contribution were excluded from the final fits. However, these positions were used to determine the real temperature of the data collection from the known platinum thermal expansion.

3. Results and discussion.

3.1. Clinkerization on heating.

Rietveld quantitative phase analyses were obtained for all the compositions and temperatures. Raw mixture of B_ref, Table 1, is used as reference material as no activators (K_2CO_3 or Na_2CO_3) were added. The amounts of Na_2O and K_2O for B_ref, given in Table 1, are due to their natural presence in the raw materials. Figure 1 shows the Rietveld quantitative phase analysis results for B_ref and B_0.5NK at each recorded temperature on heating.

At the first measured temperature, i.e. 920 °C for B_ref, a huge amount of free lime (■), 24.4(2) wt%, coexists with α'_L-C_2S (M), 68.8(2) wt%. There are also small percentages of C_3A (○) and C_4AF (ξ), 3.8(2) and 1.1(1) wt%, respectively. At 1055°C, free lime content is decreasing due to its reaction to form more aluminates and C_2S . At this temperature, the coexistence of the two polymorphs α'_L-C_2S (M) and α'_H-C_2S (8) was initially identified and finally quantified.

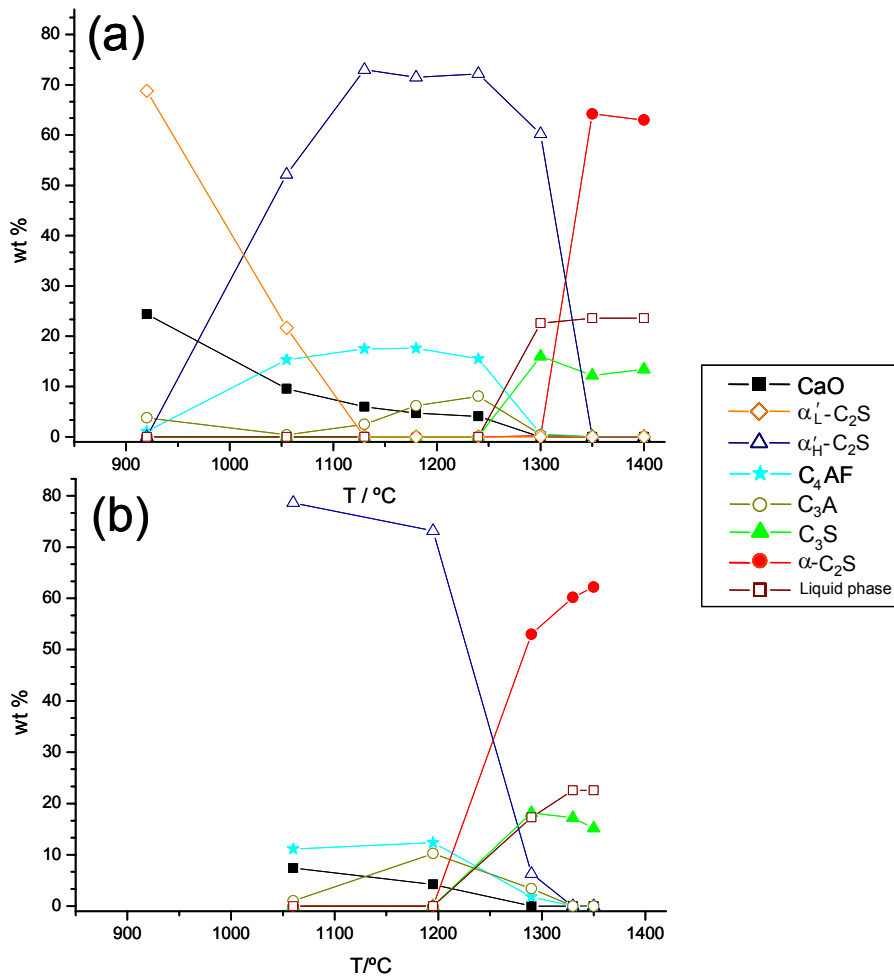


Figure 1. Rietveld quantitative phase analysis results on heating for (a) B_ref and (b) B_0.5NK.

At 1180°C complete polymorphic phase transformation, $\alpha'_L\text{-C}_2\text{S} \rightarrow \alpha'_H\text{-C}_2\text{S}$, took place. In addition to that, C_4AF phase concentration notably increases. At 1240°C, the amount of free lime is small, 4.1(1) wt% and the highest quantities of crystalline C_3A and C_4AF are formed, 8.1(2) and 15.5(3) wt% respectively. It is noticeable that at this temperature, there is a very good agreement between the theoretical composition (expected: 8.0% of C_3A and 16.0% of C_4AF) and the quantitative Rietveld results. Figure 2(a) shows a selected range of the Rietveld fit of 1240°C pattern for B_ref with the main peaks due to a given phase, labelled. Between 1240°C and 1300°C, the aluminium rich phases, C_3A and C_4AF , melt. This phenomenon is of extreme importance in clinkerization process as once the liquid phase appears, C_3S is formed from the reaction between C_2S and free lime. In Figure 2(b), a selected range of the 1350°C Rietveld plot for B_ref on heating is also given, where only the main peaks for $\alpha\text{-C}_2\text{S}$ (●) and rhomboedral C_3S (▲) are observed (and labelled).

Figure 1 also gives the amount of liquid phase (□) above 1300°C. The percentage of liquid phase (melting) was indirectly determined from the maximum values for crystalline C_3A and C_4AF on heating obtained using Rietveld methodology. For instance, in B_ref the overall liquid phase at high temperatures is assumed to be 23.6 wt%, which is the maximum percentages of C_3A and C_4AF obtained at 1240°C, see above. The overall melted aluminate fraction for B_0.5NK, see Figure 1(b), was 22.6 wt%, which was calculated from the aluminate fractions at 1195°C as previously indicated.

The polymorphic transformation $\alpha'_H\text{-C}_2\text{S} \rightarrow \alpha\text{-C}_2\text{S}$ has also been followed. For B_ref, this phase transition took place in the range of 1300°C and 1350°C. It must be highlighted that the addition of the activators in B_0.5NK slightly decreases this temperature transformation, see Figure 1(b).

3.2. Transformations on cooling.

In the overall clinkerization process, the cooling reactions are at least as important as the previously described heating transformations. The final cement performances depend upon the phase assemblage and the microstructure of those phases. These three compositions were also studied on cooling from high temperature. The patterns collected on cooling for B_1.0K sample are given in Figure 3. In Table 2, quantitative phase analysis results for this sample at all measured temperatures are given.

The highest crystalline amounts of C_3A and C_4AF at 1200°C (on heating) are given in Table 2. The amount of liquid phase for B_1.0K, 20.0 wt%, was derived from those values as indicated above.

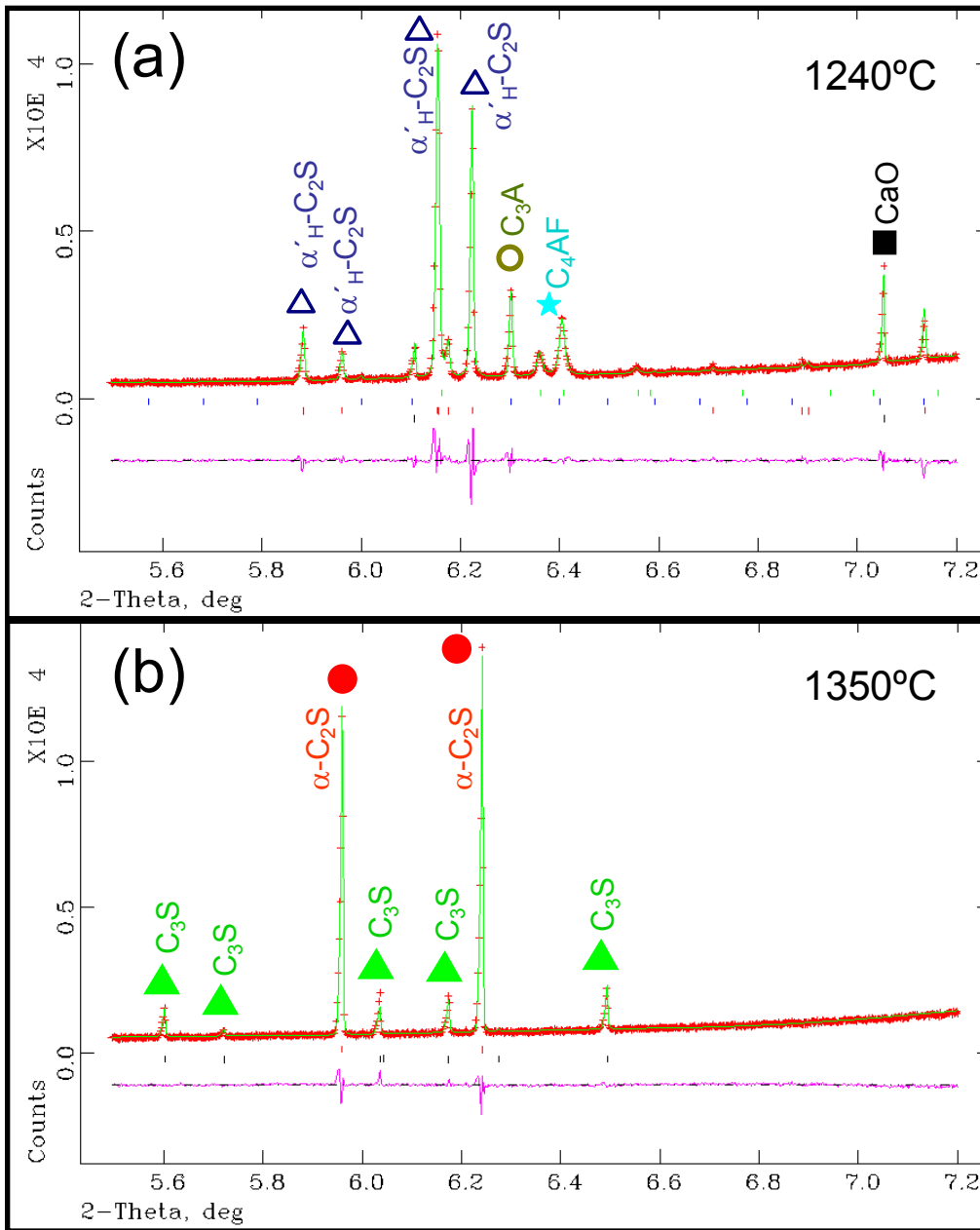


Figure 2. Selected range of the Rietveld plots for B_ref (a) 1240°C and (b) 1350°C .

In the $1440^\circ\text{C} - 1310^\circ\text{C}$ temperature range, the phase assemblage is almost constant, i.e. $\alpha\text{-C}_2\text{S}$ and rhomboedral- C_3S as crystalline phases and liquid phase, see Table 2. The complete polymorphic transformation, $\alpha\text{-C}_2\text{S} \rightarrow \alpha'_H\text{-C}_2\text{S}$ took place at 1240°C and C_3A and C_4AF started to crystallise from the melting. It must be highlighted that not all the melting crystallises at the studied temperature. The amount of aluminates (3.3

wt% of C₃A and 6.0 wt% of C₄AF) is much lower than that observed on heating. This is likely due to the fast rotation of the Pt capillaries at high temperatures. This was needed to have a good particle statistics but it very probably alters the crystallisation process. Hence, the presence of amorphous subcooled solid phase has to be introduced to properly balance the phases, see Table 2.

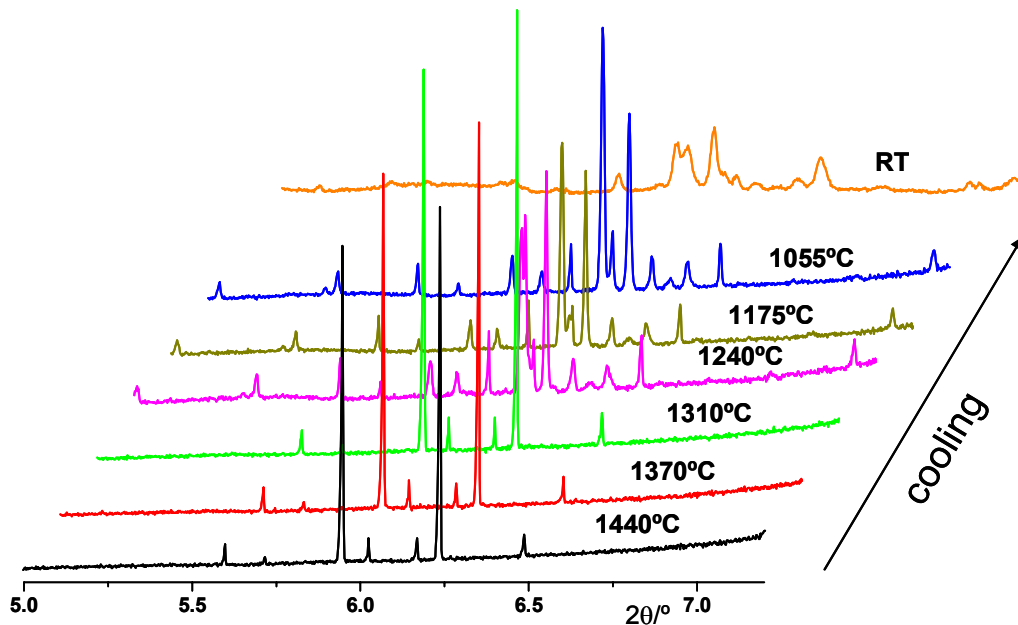


Figure 3. 3D-view of a selected range of the raw patterns for B_1.0K collected on cooling from 1440°C to room temperature.

Table 2. Rietveld quantitative phase analysis results for B_1.0K at 1200°C (on heating) and from 1440°C to 1055°C on cooling.

B_1.0K	α -C ₂ S	α' _H -C ₂ S	α' _L -C ₂ S	C ₃ S	C ₃ A	C ₄ AF	CaO	Liquid phase
1200°C	--	75.4(1)	--	--	6.0(2)	14.0(2)	4.6(1)	--
1440°C	72.7(1)	--	--	7.3(2)	--	--	--	20.0
1370°C	72.9(1)	--	--	7.1(2)	-	-	--	20.0
1310°C	72.4(1)	--	--	7.6(2)	--	--	--	20.0
1240°C	--	70.7(2)	--	9.3(2)	3.3(2)	5.6(3)	--	11.1*
1175°C	--	70.6(1)	--	9.4(2)	3.3(2)	6.2(3)	--	10.5*
1055°C	--	60.2(1)	10.3(2)	9.5(2)	3.5(1)	6.5(3)	--	10.0*

* Amorphous subcooled solid phase.

3.3. *In-situ* activation of belite clinkers.

The final objective of these studies was to better understand the clinkerization processes of belite clinkers. Some activators have been added in order to enhance hydraulic reactivity of the final materials. Figure 4 shows a selected range of the final room temperature Rietveld plots for

the three studied compositions. The phases present in these patterns were: β -C₂S, α' _H-C₂S, α -C₂S, C₃S, C₃A and C₄AF.

In B_ref no activator was added and β -C₂S form has been stabilised mainly due to the low particle sizes, so this clinker would develop low mechanical strength at early ages. The overall C₂S amount was 77.2 wt%, which is coming from 72.5 wt% of β -C₂S and 4.7 wt% of α' _H-C₂S. For B_0.5NK, the overall C₂S amount was 73.5 wt%. However, the C₂S phase assemblage was 35.9(3) wt% of β -C₂S, 34.6(2) wt% of α' _H-C₂S and 3.0(2) wt% of α -C₂S. Hence, the stabilisation of the high temperature forms of C₂S is readily observed.

It must be underlined that the volatilisation of the alkaline oxides is a very important parameter, which has not been analysed in this work. Studies characterising this behaviour (and its dependence with the overall amount of material treated) are underway. The results will be reported elsewhere.

4. Conclusions.

This *in-situ* study has allowed following polymorphic transformations of dicalcium silicate, α' _L-C₂S → α' _H-C₂S at temperatures slightly lower than 1150°C and α' _H-C₂S → α -C₂S at approximately 1300°C for all the compositions studied. Moreover, C₃A and C₄AF formation, sinterisation and melting have been followed. On the other hand, the presence of the liquid phase promotes the formation of C₃S from the reaction of C₂S and free lime in the solid-liquid interphase. Finally, the addition of activators has aided α -C₂S and α' _H-C₂S stabilisation at room temperature. These polymorphism stabilisations should enhance the slow hydration rate of Belite Portland cements.

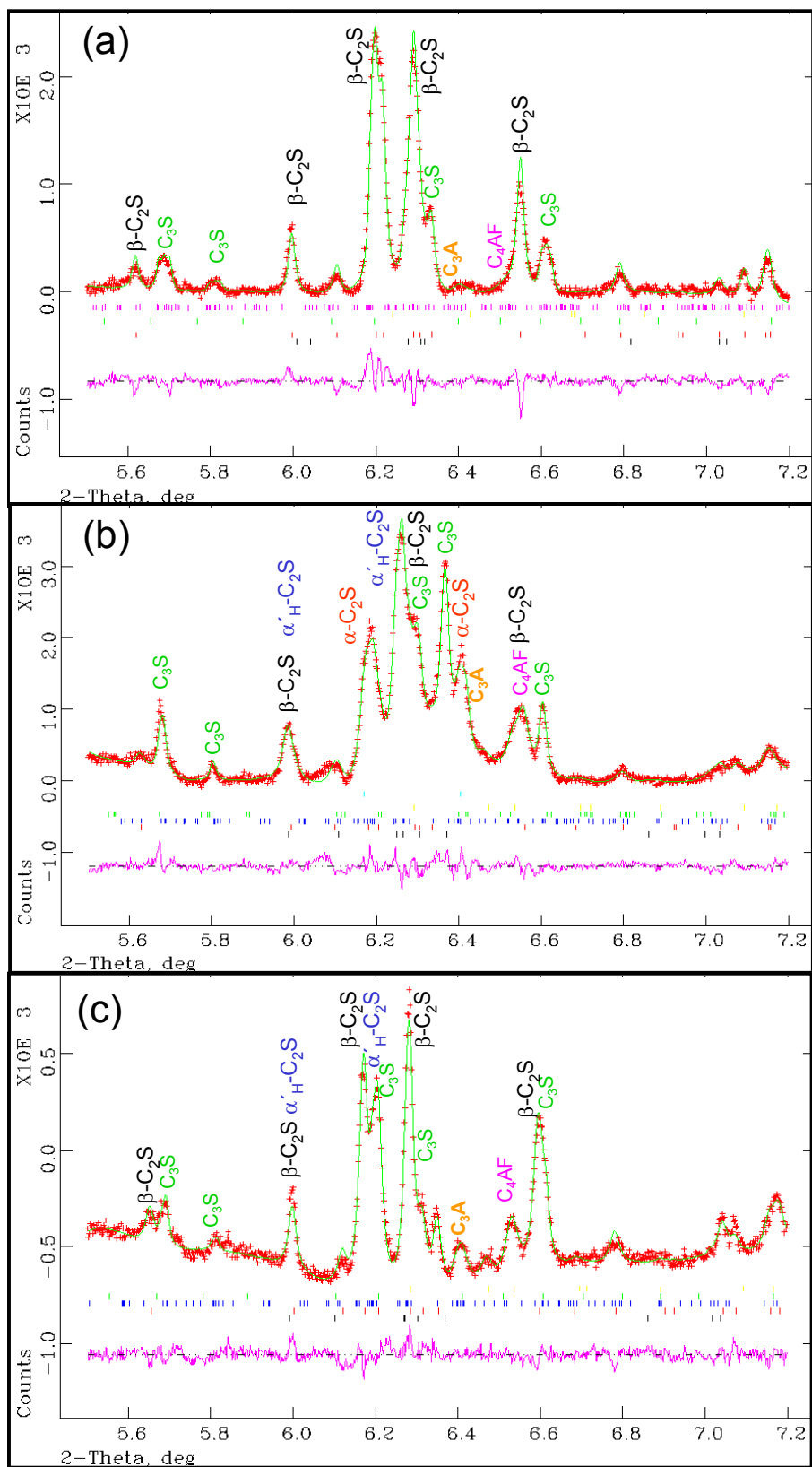


Figure 4. Selected range of the final room temperature Rietveld plots for (a) B_{ref} , (b) $B_{0.5\text{NK}}$ and (c) $B_{1.0\text{K}}$.

5. References.

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