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**PHOSPORIC ACID-BASED GEOPOLYMER FOAMS USING NATURAL LIMESTONE AS PORE
FORMING AGENT -THERMAL PROPERTIES BY *IN SITU* XRPD AND RIETVELD REFINEMENTS**

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ABSTRACT

In this work, geopolymer foams were obtained by reacting metakaolin with phosphoric acid and using natural calcite/dolomite as foaming agent. Total porosity and thermal conductivity were ca. 70 % and 0.083 ± 0.008 W/mK, respectively. Rietveld refinements, using both *ex-* and *in situ* XRPD data, were performed in order to elucidate the phase stability of the formed binder up to 1200 °C. The results showed that the amorphous matrix partially crystallized in tridymite and cristobalite type structures of $\text{AlPO}_4\text{-SiO}_2$ solid solutions at about 700 °C. At 1000°C, 3:2 mullite started to crystallize, possibly from unreacted metakaolinite, resulting in co-crystallization of SiO_2 cristobalite. At the same time, the amount of tridymite-type structure decreased, possibly due to selective phase transformation of AlPO_4 tridymite to cristobalite, leaving behind the SiO_2 isostructure. The geopolymer paste composition allows to tailor the mullite content in the refractory foam.

1. Introduction

Geopolymers are generally obtained by treating a reactive aluminosilicate precursor, such as metakaolinite or fly ash, with an alkaline sodium silicate solution at near-ambient temperature [1]. The obtained structure is amorphous, consisting of covalently bonded $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra in which the net negative charge introduced by the presence of aluminum is compensated by alkali cations [1]. About a decade ago, Wagh suggested that inorganic polymers having $[\text{PO}_4]^{3-}$ in place of $[\text{SiO}_4]^{4-}$ should be considered as a new class of geopolymers [2]. Cao et al. used various spectroscopic techniques (^{29}Si and ^{27}Al MAS-NMR, FTIR) to study metakaolinite before and after reaction with phosphoric acid [3]. Based on the observed results, the authors claimed that the reaction occurs mainly between the phosphate tetrahedral unit and the Al-O layer in metakaolinite, thus forming a three-dimensional network [3]. The model proposed by the authors thus involves metakaolinite particles bonded together by oxygen-bridged Al and P in tetrahedral coordination [3], which eliminates the need of extra-framework charge-compensating cations. The material thus acquires new interesting properties such as low dielectric loss [4].

In recent years, geopolymer foam has attracted attention from the scientific community due to high potential as green alternative to conventional foams based on ordinary Portland cement [5], and as precursor for the production of refractory foams [6, 7].

The techniques used to produce geopolymer foams are analogous to those applied for conventional foamed concretes [5]; (i) addition of a gas forming agent in the fresh paste [8-15] (ii) air-entrainment by direct addition of a preformed foam [16]. In scientific studies, the most common gas forming agents are aluminum powder [8-11], metallic silicon (added as fumed silica which contains metallic silicon as impurity) [12-13] and hydrogen peroxide [14, 15]. Another interesting technique recently presented as a viable approach for the production of porous geopolymers is emulsion templating [17,18].

In a recent review on geopolymer foam, it was pointed out that the economical/environmental benefits of geopolymer foam concrete over conventional OPC foam concrete may be compromised if high dosages of common pore forming agents (i.e. Al powder, fumed silica) with high embodied energy are used [5]. An alternative to low doses of these expensive additives may be replacement with other more economically advantageous ones [5]. Common pore forming agents for the preparation of metal foams [19] and glass foams [20] are carbonates. When the carbonate-containing melts are exposed to temperatures higher than the decomposition temperature of the carbonates, CO₂ evolves and gives rise to a porous structure. The pore forming action of these compounds can also rely on chemical decomposition at near-ambient temperature, for example when used for the preparation of porous metal phosphate ceramics [21, 22].

Limited work has been aimed to study the phase evolution of phosphorus-based geopolymers [23]. Liu et al. studied the high-temperature behavior of geopolymers obtained by reaction between a pure aluminosilicate and phosphoric acid [23]. The results obtained for the chemically pure starting material in that work are perhaps not comparable to results obtained for geopolymers prepared using conventional raw materials such as metakaolin.

In this work, inorganic foams were prepared by reaction of metakaolin with phosphoric acid using natural limestone as pore forming agent. The amount of foaming agent was kept fixed while the molar composition of the paste was varied. The changes in mineralogical composition, effective thermal conductivity (λ_{eff}) and total porosity of the foams following exposure to high temperatures (800-1000°C) were determined. In addition, special emphasis was paid to the phase evolution of the as-synthesized geopolymers. The proposed method is promising for the preparation of inorganic insulation material at near-ambient temperatures with may be transformed into an aluminum phosphate/mullite ceramic with tailored phase composition for high-temperature applications.

2. Experimental

2.1. Sample preparation

The procedure for the preparation of fumed geopolymer concrete was as follows: The desired proportions of industrial metakaolin (MK, Sibelco, Italy), orthophosphoric acid (85%, Carlo Erba) and double-distilled water were carefully mixed to obtain a homogeneous base paste. Following homogenization, a fixed amount of a liquid nonionic surfactant (Marlipal) was added (0.16 grams per 100 g of MK). Subsequently, a limestone slurry was rapidly mixed with the paste resulting in expansion. This slurry was prepared in a previous step by dispersing limestone powder in a part of the desired water content of the base paste composition. To increase disaggregation, a small amount of deflocculant (Hexametaphosphate, Carlo Erba) was also added. The amount of limestone was 4 g for each 100 g of MK. A total of 13 different pastes were prepared according to an experimental plan generated by the software Design-Expert v. 6.0.10 (Stat-ease Inc) in which the factors wt.% deflocculant, MK/water ratio and MK/H₃PO₄ ratio were varied in the ranges 0-0.5, 1.19-1.39 and 2.02-3.75, respectively. The deflocculant used for the limestone slurry was also included as a variable in order to assure that this additive did not affect the technological properties of the hardened material. The investigated compositions are shown in Table 1.

The expanding geopolymer pastes were directly cast in cylindrical (height 12 cm, diameter 3.76 cm) polyethylene molds, three for each investigated composition. A lubricated polymer rod was inserted in the center of each cylinder in order to create a hole which served to accommodate the sensor for thermal conductivity (λ_{eff}) measurements that will be described later. The filled molds were left at ambient temperature for about 1h after which they were sealed and put in an electrical furnace holding a temperature of 60 °C. After 24 h, the sealed molds were left at ambient temperature for 28 days. Following curing, the samples were

extracted from the molds, dried at 80 °C for 96 h and consequently kept in a dessicator prior to further treatment.

2.2. Analysis techniques

The chemical composition of metakaolin was determined by X-ray fluorescence spectroscopy (XRF, Philips PW 1480).

The BET specific surface area of the raw materials was measured using a Gemini 2360 (Micromeritics) instrument. Nitrogen (high purity grade) was used as probe gas.

The grain size distribution of the limestone used as pore forming agent was determined using a laser granulometer (Mastersizer 2000, Malvern Instruments) equipped with a system for measurement in humid (Hydro 2000S). Deionized water was used as carrier fluid.

Calcimetry (Dietrich-Fruhling apparatus) was used to determine the carbonate content in the limestone.

The bulk densities (ρ) of dry geopolymer specimens were determined by weight and geometrical calculations of dry samples (24 h at 105 °C).

The true densities (ρ_t) were determined using a gas displacement pycnometer (AccuPyc 1330, Micromeritics Inc., USA). Samples were ground to fine powders and consequently dried (24h at 105 °C) prior to analyses.

The total porosity (TP , %) was calculated according to [24]:

$$TP = \left(1 - \frac{\rho}{\rho_t} \right) \cdot 100 \quad (2)$$

Scanning electron microscopy (SEM) analyses were performed using an environmental SEM (ESEM Quanta-200, FEI company) equipped with a INCA-350 (Oxford Instruments) energy-

150 dispersive X-ray spectroscopy analysis system. For SEM analyses, polished cross-sections of
151 hardened geopolymers were prepared as follows: In the first step, each sample was
152 impregnated with epoxy resin. Following hardening of the resin, sequential rough polishing
153 was performed using 240-2000 mesh grade SiC abrasive paper. In the last step, mirror finish
154 was accomplished using 2.5 and 0.5 μm diamond pastes. The polished samples were
155 consequently washed in acetone and dried at 40 °C. The washed and dried samples were
156 mounted on aluminum stubs gold coated (10 nm) prior to electron microscopy observations.
157 Transmission electron microscopy analyses (TEM) were performed on ceramic foams using a
158 Jeol JEM 2010 instrument working at 200 kV. The foams were gently crushed and the
159 resulting powder was dispersed in distilled water. Following ultrasonification for ca. 1h,
160 particles were collected on a Cu grid sample holder and dried.

161 Simultaneous thermal analyses (TG/DTA) were performed in air (Pt crucible, 20 °C/min
162 heating rate up to 1400 °C) using a STA 429 CD instrument (Netzsch, Geraetebau GmbH,
163 Germany).

164 X-ray powder diffraction (XRPD) data were collected using a θ/θ diffractometer
165 (PANalytical, $\text{CuK}\alpha$ radiation), equipped with an Anton Paar HTK 16 resistance heating
166 chamber. A real time multiple strip (RTMS) detector allowed fast data acquisition. The
167 incident beam pathway included a soller slit (0.04 rad) as well as divergence and anti-
168 scattering slits. These slits had an opening of 0.5°. The pathway of the diffracted beam
169 included a Ni filter, a soller slit (0.04 rad) and an antiscatter blade (5 mm). A virtual step scan
170 (0.0167 °2 θ) was performed in the range 3-90 °2 θ .

171 Samples for *ex-situ* data collection were carefully ground and mounted in aluminium sample
172 holders using side-loading.

173 *In situ* data were collected for both cured geopolymer sample (composition 3 in Table 1) and
174 heat-treated (800 °C and 1000°C) counterparts. The temperature on the heating strip,
175 functioning as sample holder, was calibrated against known phase transitions and phase

176 decompositions. All experiments were performed in air using a heating rate of 20 °/min. For
177 as-synthesized and cured samples, data were collected in the range 15-50 °2 θ using an
178 acquisition time of 3 min. Instead, data for heat-treated samples were collected in the range
179 15-65 °2 θ using an acquisition time of about 11 min. The faster data collection in the former
180 case was chosen to more closely mimic the continuous heating ramp applied in the TG/DTA
181 analyses of the same sample.

182 Full quantitative phase analyses were performed using XRPD data and Rietveld refinements.
183 The software used were GSAS [25] and its graphical interface EXPGUI [26]. The refinement
184 strategy was adopted from previous work, including calibration of instrumental and profile
185 parameters [27]. Samples for FQPA were mixed with a known amount of internal standard
186 (10 wt% corundum NIST 676a) which was treated as part of the sample in subsequent
187 Rietveld refinement analyses. Elaboration of data extracted from Rietveld refinements was
188 performed according to the procedures previously described in detail [28].

189 Accurate unit cell parameters of the constituting crystalline phases could be followed in
190 temperature (*in situ* data) by using a standard silicon powder (NIST 640c) directly mixed in
191 the sample. The correct unit cell of the Si standard at each temperature, calculated using the
192 certified unit cell at RT and known thermal expansion [29], was fixed in the Rietveld
193 refinements in order to correct for zero offset as well as sample displacement due to thermal
194 expansion of the sample holder. The structure models of the main phases used for the
195 refinements were: α -Al₂O₃ [30]; triclinic low-tridymite structure in space group *F1* [31];
196 tetragonal low-cristobalite structure in space group *P4₁2₁2* [32], cubic high-cristobalite in
197 spacegroup *Fd-3m* [33]; low-quartz in space group *P3₂21* [34], mullite in spacegroup *Pbam*
198 [35]. Tridymite present in calcined samples at RT fits well with the triclinic structure (space
199 group *F1*) described by Graetsch [31]. However, already at 113 °C, the 240 peak present at
200 about 27.2 °2 θ disappears, indicating a phase transition to higher symmetry. It is well-known
201 that the tridymite structure displays a sequence of phase transitions during heating [36,37,38].

However, for sake of simplicity and difficulty to identify the various temperature-induced modifications, tridymite was refined in space group *F1* at all investigated temperatures. Mercury porosimetry data were collected using an Autopore IV 9500 scanning mercury porosimeter (maximum pressure 33000 psia, pore size range 0.005-360 μ m). The contact angle and surface tension of mercury were set at 130° and 485 dynes/cm, respectively. Prior to analyses, samples were dried at 110 °C for 24 h and consequently kept in a dessicator. Effective thermal conductivity (λ_{eff}) measurements at 28 °C were performed using a KD2 Pro Thermal properties analyzer (Decagon Devices, Inc) equipped with a TR-1 sensor needle. Thermal grease was used to reduce contact resistance between the sensor and the material.

3. Results and Discussions

3.1 General characterization of the starting material

Figure 1 shows the XRD patterns for metakaolin used as raw material for sample preparation (a) as well as the natural limestone used as pore forming agent (b). The metakaolin exhibits the typical background bump associated with metakaolinite [39] and contains quartz, muscovite/illite and microcline as minor crystalline phases. FQPA results obtained using an internal standard and the Rietveld method (see experimental) are shown in Table 2, together with results from chemical analysis. Although some degree of long-range order is preserved in metakaolinite [39], it is reasonable to treat this phase as being completely amorphous in the FQPA. As shown in Table 2, the amorphous content in the metakaolin amounts to 82 wt.%, most probably assigned to the metakaolinite content.

The natural limestone used as pore forming agent contains calcite and dolomite with a trace amount of quartz. Semi-quantitative phase analysis with XRPD data (see Figure 1) and the Rietveld method gave the following mineralogical composition: 14.1 $\pm$ 0.1 Wt.% dolomite;

85.4 ± 0.1Wt.% calcite; 0.5 ± 0.1 Wt.% quartz. The amount of carbonates is in good agreement with the calcimetry results that gave a total carbonate content of 99 Wt.%. The grain size distribution of metakaolin, determined by laser diffraction showed D(50) and D(90) was 2.8 µm and 8.3 µm, respectively. The corresponding values for the natural limestone was 5.3 µm and 16.7 µm .

3.2. Macroscopic properties of inorganic foams

3.2.1 Geopolymer foams

Table 3 shows the results from the various measurements performed on the hardened and dried samples (ρ_t =true density, ρ =bulk density, TP=total porosity, λ_{eff} =effective thermal conductivity). The porosity range of the samples obtained from the different compositions is very narrow, being 69-76 %. As a consequence, the λ_{eff} range is also narrow (0.07-0.09 W/mK). No statistically relevant correlations could be found between the independent parameters and the macroscopic properties of the resulting samples. Controlled addition of the pore forming agent is generally used to tailor the porosity created in the hardened matrix [8]. In the work presented here, the weight ratio MK/limestone was kept fixed and low enough to guarantee bubble saturation of the fresh paste. Hence, the obtained porosity probably represent the upper limit at which a continuous solid skeleton is formed. Figure 2 shows low-magnification BSE images of polished cross-sections of two typical samples representing the general distribution of the macroporosity created by the pore forming agent. The selected magnification allows to quantify pores in the approximate size range 100-3000 µm. Although difficult to evaluate, it appears that the porous structure was created by coalesced gas bubbles, leading to high pore interconnectivity in the hardened structure. Some samples display large round-shaped pores (for example sample 10 displayed

in Figure 2a) whereas other samples have smaller interconnected pores (for example sample 3 in Figure 2b). Image analyses using the free-ware ImageJ [40] of five representative BSE images of each sample were performed. The mean value of the Feret's diameter for sample 3 and 10 was found to be 0.46 and 0.55 mm, respectively. The size distribution of pores smaller than the ones observable in the BSE images in Figure 2 were determined by mercury intrusion experiments and will be discussed later (section 3.2.2.).

Qualitative analyses of the as-prepared samples (not shown here) evidenced an important background signal in all diffractograms, indicative of amorphous material. In fact, similar to alkali-activated metakaolinite, lack of long-range order is expected in geopolymeric material obtained from reaction between metakaolinite and phosphoric acid [3]. Crystalline phases include quartz and muscovite/illite, already present in the metakaolin used as raw material (see Table 2), and newly-formed tridymite-type structure in some samples. As an example, FQPA of sample 3 was performed and the following weight composition was obtained: quartz 9.3 ± 0.1 ; tridymite-type structure 1.5 ± 0.2 ; muscovite/illite 2.7 ± 0.2 ; amorphous 86.5 ± 0.2 . The Rietveld refinement output is shown in Figure 3 where the observed, calculated and difference curves are depicted.

3.2.2. Ceramic foams by firing of geopolymer precursor foam

Figure 4 shows the true density (a), bulk density (b), total porosity (c) and effective thermal conductivity (d) of the heat-treated samples as a function of the corresponding values for the as-prepared samples. It should be pointed out that only one sample for each batch was heat-treated and the data shown in Figure 4 corresponds to the exact values obtained for that sample before and after heat-treatment.

Without exceptions, the true density apparently increased following heat-treatment, probably due to crystallization of the amorphous phase into a more dense structure. Generally speaking, the bulk density also increased with the exception of a couple of points at the high and low

density-regions of the curve (Figure 4b). Heating at 1000 °C resulted in a structure with higher total porosity (see Figure 4c) and up to threefold higher λ_{eff} (see Figure 4d). Although increased porosity accompanied with higher λ_{eff} could be considered a paradox, the results are surely explained by densification of the solid skeleton.

Mercury intrusion experiments were performed to evaluate the heat-induced changes of the porous network for samples having compositions 3 and 10, showing different types of macropores in the as-prepared state (see BSE images in Figure 2). The total intrusion volume before and after calcination for sample 3 was 0.4486 and 0.4797 mL/g, respectively. The corresponding values for sample 10 were 0.5554 and 0.5615 mL/g. The porosity of sample 3 increased from 49.79 to 51.53 % following calcination. An increase in porosity, from 55.17 to 57.40 %, was also observed for sample 10. Generally speaking, the porosity values are lower than the ones determined by eq. 2 (compare with data reported in Figure 4c). This is possibly explained by the presence of closed porosity (thus not accessible to mercury) and/or pores having sizes out of the measurement range of the instrument (i.e. 0.005-360 μm). In fact, most macropores observed in the low-magnification SEM images depicted in Figure 2, are too large to be evaluated. Nevertheless, the increase in porosity following calcination observed in the data plotted in Figure 4c is confirmed. Figures 5a and 5b show $dV/d\log D$ (V =volume of intruded mercury) and the cumulative pore volume as a function of pore diameter (D), for sample 3 and 10, respectively. The pore size was calculated using the classical Washburn equation [41]. Data from both as-prepared and calcined samples are depicted. The pore size distribution is bimodal, having peaks at about 0.1-0.3 μm and 120-140 μm . The larger pores, also detectible in the BSE images displayed in Figure 2, were probably created by the poreforming agent. The smaller macro/meso pores are most probably associated with the geopolymer phase, although larger than the ones normally observed for alkali-activated metakaolin [8]. In fact, the mean size of gel pores in inorganic cements obtained by geopolymerization of metakaolin in an alkaline environment is generally in the meso-pore range [8]. The lack of fine pores in phosphate geopolymers obtained from laterite was also recently reported [42]. The most important change in the porous network after calcination is observed in the small pores. In fact, a shift towards higher values are observed for both samples. This is not surprising as the geopolymer phase exhibits important mineralogical changes following calcination, as will be discussed below.

Table 4 and Table 5 show the FQPA results and the results from chemical analyses, respectively, of each composition following calcination at 1000 °C for 3h. As can be observed from table 4, newly-formed phases are tridymite, cristobalite and mullite. Small amounts of whitlockite could also be detected, surely originating from the reaction between phosphoric acid and the pore forming agent (natural limestone). No statistically relevant correlations could be found between the independent parameters and the macroscopic properties of the resulting samples, apart from a clear positive linear trend between the amount of formed mullite and the MK/acid ratio. Consequently, a linear trend was also found between mullite and the amount of P_2O_5 from the chemical analyses. The increased mullite content with decreasing amount of phosphoric acid is probably related to less reacted metakaolinite which consequently is available for mullite crystallization. It is thus possible to tailor the amount of mullite in the calcined material by adjusting the composition of the initial geopolymer paste. $AlPO_4$ is isomorphous with silica and may crystallize in its various polymorphs (quartz, tridymite, cristobalite). It is difficult to distinguish the different isomorphs due to highly similar powder diffraction patterns. The chemical compositions were calculated based on stoichiometric formula and the FQPA results presented in Table 4, assuming crystallization of $AlPO_4$ cristobalite and tridymite, and compared to the XRF analyses (Table 5). It was found that the amounts of Al_2O_3 and P_2O_5 were severely overestimated, indicating that the cristobalite and/or tridymite also appears as silica and/or solid solutions of the two isostructures. Considering the model for geopolymerization of metakaolinite by reaction with phosphoric acid suggested by Cao et al. [3] (see introduction), the proposed structure indeed results in a blend of Al, P and Si on a molecular level. Hence, crystallization of solid solutions of the two isomorphs is possible. In order to elucidate the thermal behaviour of the geopolymer phase, TG/DTA analyses and an extensive XRPD investigation were conducted. The results of these analyses will be discussed in the following section.

3.3. Thermal phase transformations/transitions

Figure 6 shows the results of the thermogravimetric analysis of a powder specimen obtained from a sample having composition 3 (see Table 1). A significant weight loss (ca. 14.4 %), accompanied by a broad endothermic DTA peak at 154 °C, was observed in the temperature range 25-300 °C and assigned to dehydration. The second thermal event, observed at 694 °C, is exothermic and assigned to crystallization of the amorphous matrix into cristobalite and tridymite-type structures (see below). Another exothermic peak is observed at 1004 °C, assigned to mullite crystallization (see below). Figure 7 shows *in-situ* XRPD data (650-960 °C) collected for the same sample and results from quantitative phase analyses using the known amount of intrinsic quartz as internal standard. As can be observed, tridymite- and cristobalite-type structures simultaneously crystallize from the amorphous phase already at the first investigated data point (650 °C). No further increase in quantity of these phases is observed above 720 °C. It is thus probable that the exothermic reaction observed at 694 °C in the DTA trace (Figure 6) is due to the simultaneous crystallization of tridymite-type and cristobalite-type structures.

Figure 8 shows ex-situ XRPD diffraction patterns collected from sample 3 (same as above) following calcination for 3 h at three different temperatures (800, 900 and 1000 °C). The identified phases, apart from quartz already present in the starting material, are tridymite- and cristobalite-type structures as well as mullite, the latter not appearing until a temperature of 1000 °C is reached. Figure 9 shows the FQPA results of the major constituting phases as a function of calcination temperature. For comparison, the results of the as-prepared sample is also displayed. As can be observed, the amounts of tridymite- and cristobalite-type structures increase up to 900 °C on the expense of the amorphous phase which decreases. At 1000 °C, mullite starts to crystallize. The amount of cristobalite-type structure drastically increases from 12±0.2 to 32.3±0.5 wt% whereas the opposite is observed for tridymite-type structure (from 38.5±0.5 to 24.9±0.5 wt%) and amorphous phase (from 40.0±0.6 to 21.2±0.9 wt%). In

order to explain these results, the chemical composition of mullite is needed and can be determined by the unit cell parameters accurately determined in this work. Mullite is a solid solution of alumina and silica with stoichiometries ranging from $3\text{Al}_2\text{O}_3:2\text{SiO}_2$ (3:2 mullite) to $2\text{Al}_2\text{O}_3:\text{SiO}_2$ (2:1 mullite) [43]. According to Ban and Okada [44], the stoichiometry is related to the length of the a -axis (nm) according to the following empirical expression:

$$\text{Al}_2\text{O}_3 \text{ (mol\%)} = 1443 \times a - 1028.06$$

Applying this relationship to the sample investigated here gave 61.3 ± 0.9 mol% Al_2O_3 . Hence, the mullite crystallized in the system studied here is close to the high-silica extreme (i.e. 3:2 mullite). Stoichiometric calculations show that crystallization of 13.3 wt.% 3:2 mullite from metakaolinite results in a 20.8 wt.% decrease in amorphous content and a 7.5 wt.% increase in silica. The expected decrease in amorphous content is thus in rather good agreement with the observed one (18.8 wt.%, see Figure 9). The increase in cristobalite content of 20.3 % is explained by co-crystallization with mullite (7.5 wt%) and recrystallization of tridymite-structure to cristobalite-type structure (13.6 wt.%, see Figure 9). If this assumption is correct, the cristobalite-type phase present following high-temperature treatment at 1000°C should, a part from the $\text{AlPO}_4:\text{SiO}_2$ cristobalite solid solution, also include the pure SiO_2 isostructure. A possible way to investigate this further is to compare the unit cell volume as a function of temperature for the same sample treated at 1000 °C and 800 °C. In the latter case, the amount of silica cristobalite should be minor with respect to the one obtained after calcination at 1000 °C. According to the literature, such changes should result in important effects on the unit cell dimensions. In fact, the unit cell volume of silica cristobalite is smaller than the one found for AlPO_4 cristobalite [45,46].

Figure 10a shows the unit cell volume as a function of temperature for cristobalite. For comparison, data for solid solutions in the cristobalite system $\text{AlPO}_4\text{-SiO}_2$ determined by Horn and Hummel [47] are also shown together with the corresponding curves for the pure extremes determined by Wright and Leadbetter [48]. First of all, phase transitions are usually

accompanied by a change in volume. In fact, the phase transition from α - to β -cristobalite is evident in the X-ray powder patterns mainly due to a sudden peak shift to lower 2θ . In this work, this change was observed already at 113 °C (see Figure 10a), which is considerably lower than the transition temperature normally observed for pure silica structures (200-275 °C [49]). Considering the low chemical purity of the system under study, containing both alkaline and alkaline earth metals as well as phosphate, incorporation of e.g. Na and Ca as well as AlPO_4 in the framework structure is expected and known to affect the transition temperature and even stabilize β -cristobalite at RT [50]. According to Horn and Hummel [47], the thermal expansion curves of SiO_2 and AlPO_4 cristobalite are not much affected by the inclusion of AlPO_4 and SiO_2 in the respective phase (see Figure 10a). Interestingly, the curve determined for a sample precalcined at 1000 °C lies between the AlPO_4 and SiO_2 extreme, whereas the sample precalcined at 800 °C is close to the $\text{AlPO}_4/\text{AlPO}_4\text{-SiO}_2$ cristobalite structures (see Figure 10a). The most probable explanation is that the two cristobalite structures are **exsolved, resulting** in a unit cell volume vs. temperature curve that represents an average of the unit cell volume of the two phases.

Figure 10b shows the unit cell volume as a function of temperature for tridymite and quartz. In contrast to cristobalite, tridymite exhibits several phase transition with only very small changes in unit cell volume and therefore difficult to identify by thermal expansion curves [37]. Nevertheless, the phase transition from orthorhombic to hexagonal structure is rather clearly identified by a sudden change in thermal expansion [36, 37, 50], which in this work was observed at about 160 °C, see Figure 10b. Again the much lower phase transition temperature observed in this work, compared to pure silica tridymite (ca 350 °C [37, 51]) is not surprising as the transition temperatures are shifted to lower values for AlPO_4 tridymite. In addition, the thermal behaviour of tridymite is sensitive to structural defects such as stacking faults and interstitial cations in the framework [37]. The transition from α -quartz to

β -quartz is evident in Figure 10b as a sudden change in thermal expansion and is known to occur at a temperature of 573 °C [52]. From Figure 10b, it can be observed that the only difference between the tridymite unit cell volume vs. temperature curves collected for a sample annealed at 800 °C and 1000 °C is that the latter is shifted to lower values. A possible explanation, though needing further supporting evidence, is recrystallization of AlPO_4 tridymite to cristobalite at temperatures higher than 1000 °C, leaving behind a structure enriched in silica with a smaller unit cell. The thermal expansion of quartz remain practically invariant as expected (see Figure 10b), indicating a correct analysis.

Supporting evidence for the events described above were sought in TEM analyses. Figure 11 shows images of sample 3 (same as above) following calcination at 1000 °C. Thin hexagonal platelets of tridymite were identified (indicated with A). Round-shaped particles (indicated by B) composed of Al, P and Si were observed, the molar ratio of the two former elements being 1 indicating an AlPO_4 phase. P-depleted thin flakes with a granular surface are observed (indicated with C) and are possibly SiO_2 -rich tridymite relicts left behind following recrystallization of AlPO_4 tridymite to cristobalite as suggested from the thermal expansion curves discussed above (see Figure 10b). Needle-shaped mullite crystals, indicated by D in Figure 11d, were observed.

In light of the results presented above, the following model for thermal phase evolution of geopolymers based on metakaolinite and phosphoric acid is proposed: Upon heating, the amorphous geopolymer crystallizes into tridymite-type and cristobalite-type structures, resulting in an exothermic DTA peak at 690 °C. The formed structures at this temperature are most likely solid solutions of AlPO_4 and SiO_2 since the calculated chemical composition based on the FQPA results assuming pure AlPO_4 phases results in an overestimation of P_2O_5 compared to the XRF chemical analyses. This assumption is further supported by the fact that the unit cell volume vs. temperature curve of cristobalite is close to literature values of AlPO_4 - SiO_2 solid solutions. When higher temperatures are reached (>1000 °C), the

cristobalite content drastically increases due to thermal transformation of unreacted metakaolinite to 3:2 mullite, thus releasing residual silica. Hence, the cristobalite structure at this temperature is a mixture of $\text{AlPO}_4\text{-SiO}_2$ solid solution and the pure SiO_2 isostructure. This conclusion is again based on the unit cell vs. temperature curve which in this case is positioned between the one expected for $\text{AlPO}_4\text{-SiO}_2$ solid solutions and the pure SiO_2 structure. Instead, the amount of tridymite-type structure decreases following calcination at 1000 °C. This is possibly explained by selective phase transformation of AlPO_4 tridymite to cristobalite leaving behind the SiO_2 isostructure. In fact, the unit cell volume vs. temperature curve is shifted to lower values with respect to a sample calcined at lower temperature (800°C).

Liu et al. studied the high-temperature behavior of geopolymers obtained by reaction of a pure aluminosilicate and phosphoric acid [10]. Qualitative evaluations of XRD patterns collected from fired samples showed that the amorphous geopolymer started to crystallize at 900 °C, thus forming quartz and berlinite. At higher temperatures (>1150 °C), cristobalite and mullite crystallized. In addition, orthorhombic aluminum phosphate also appeared. The important differences observed in phase evolution between the samples studied by Liu et al. and the ones studied in the present work demonstrate that phase stability and thermal transformations in phosphate geopolymers may differ depending on the starting material. In particular, the chemical composition (possible atomic substitutions which might stabilize metastable structures) and chemical homogeneity (e.g degree of geopolymerization, linking of tetrahedral units) are surely important.

4. Conclusions

In this work, natural limestone was used as pore forming agent in the preparation of foamed geopolymer with high porosity (68-70%) and low thermal conductivity (0.092-0.095 W/mK). The adopted synthesis approach included activation of metakaolinite with phosphoric acid,

leading to an amorphous binder phase. The acidic environment of the fresh paste provoked chemical decomposition of added carbonates with gas release (CO₂) and consequent foam formation. Thermal and microstructural properties were investigated to shed light on the chemico-physical nature of the foamed geopolymer. In particular, *in situ* XRPD and Rietveld refinements gave accurate thermal expansion curves and quantitative phase analysis data of the constituting phases. Following firing at 1000 °C, the total porosity slightly increased whereas λ_{eff} more than doubled due to partial crystallization and consequent densification of the solid skeleton. The hardened amorphous structure partially crystallized in tridymite-type and cristobalite-type AlPO₄-SiO₂ solid solutions at a temperature of about 700 °C. At 1000 °C, mullite started to crystallize, probably from non-reacted metakaolinite leading to crystallization of residual SiO₂ to cristobalite. In concomitance with this event, phase transformation of AlPO₄ tridymite-type to cristobalite-type structure likely occurred, leaving behind the SiO₂ tridymite isostructure. The carbonate, present in amorphous form in the non-heated geopolymer, crystallized into β -Ca₃PO₄.

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TABLES

Table 1. Composition of investigated base pastes, according to a 2 level factorial design with 5 centerpoints.

Sample	* wt.% deflocculant	MK/H ₂ O	MK/H ₃ PO ₄	deflocculant	Weight composition				
					H ₃ PO ₄ (85 wt.%)	H ₂ O	MK	lime stone	surfactant
1	0	1.2	2.0	0	53.5	75.3	100	4	0.16
2	0.5	1.2	2.0	0.5	53.5	75.3	100	4	0.16
3	0	1.4	2.0	0	53.5	63.4	100	4	0.16
4	0.5	1.4	2.0	0.5	53.5	63.4	100	4	0.16
5	0	1.2	3.8	0	26.7	79.3	100	4	0.16
6	0.5	1.2	3.8	0.5	26.7	79.3	100	4	0.16
7	0	1.4	3.8	0	26.7	67.4	100	4	0.16
8	0.5	1.4	3.8	0.5	26.7	67.4	100	4	0.16
9	0.25	1.3	2.9	0.25	35.6	71.6	100	4	0.16
10	0.25	1.3	2.9	0.25	35.6	71.6	100	4	0.16
11	0.25	1.3	2.9	0.25	35.6	71.6	100	4	0.16
12	0.25	1.3	2.9	0.25	35.6	71.6	100	4	0.16
13	0.25	1.3	2.9	0.25	35.6	71.6	100	4	0.16

*with respect to MK

Table 2. Chemical and mineralogical composition, determined by XRF and FQPA, of industrial metakaolin used for sample preparation.

Chemical composition (wt.%)										
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MgO	K ₂ O	CaO	Cr ₂ O ₃	Na ₂ O	MnO	L.O.I.
59.45	37.24	0.77	0.46	0.51	1.02	0.42	0.01	0.67	0.01	1.3
*Mineralogical composition (wt.%)										
quartz		muscovite/illite			microcline			amorphous		
13.2 ± 0.3		4.5 ± 0.2			0.7 ± 0.1			81.6 ± 0.4		

*Anatase and hematite in trace amounts (< 0.5%)

Table 3. Various macroscopic properties (ρ_t =true density, ρ = bulk density, TP= total porosity, TC=thermal conductivity) of as-prepared samples based on the paste compositions presented in Table 2.

Sample	ρ_t (g/cm ³)	ρ (g/cm ³)	TP (%)	TC (W/mK)
1	2.323±0.002	0.60±0.06	74±2	0.08±0.02
2	2.290±0.004	0.6±0.1	75±4	0.07±0.02
3	2.299±0.004	0.7±0.2	69±8	0.09±0.01
4	2.326±0.004	0.73±0.06	69±3	0.073±0.004
5	2.370±0.004	0.61±0.05	74±4	0.089±0.008
6	2.375±0.003	0.67±0.07	72±3	0.09±0.01
7	2.373±0.004	0.67±0.07	72±3	0.090±0.007
8	2.388±0.005	0.6±0.1	74±4	0.08±0.01
9	2.351±0.004	0.58±0.05	76±2	0.08±0.02
10	2.337±0.004	0.70±0.05	70±2	0.091±0.005
11	2.355±0.002	0.63±0.05	72±2	0.07±0.01
12	2.355±0.005	0.6±0.1	73±5	0.09±0.03
13	2.334±0.004	0.6±0.1	73±5	0.08±0.01

Table 4. FQPA results for each investigated composition following calcination at 1000 °C for 3h.

Sample	Mineralogical composition (wt.%)					
	tridymite-type	cristobalite-type	mullite	quartz	whitlockite	amorphous
1	19.4±0.3	37.1±0.3	11.2±0.4	11.2±0.4	0.97±0.09	25.1±0.6
2	30.0±0.4	30.2±0.4	12.6±0.6	8.5±0.1	*	18.4±0.8
3	24.9±0.5	32.2±0.5	13.3±0.4	7.7±0.2	0.3±0.1	21.2±0.9
4	25.3±0.3	33.0±0.3	14.0±0.5	7.2±0.1	1.1±0.1	11.6±0.4
5	22.7±0.3	25.3±0.3	24.0±0.3	7.5±0.1	*	20.6±0.5
6	23.9±0.3	22.4±0.3	23.7±0.3	8.4±0.1	*	21.5±0.5
7	20.2±0.3	22.1±0.2	22.1±0.3	8.3±0.1	0.34±0.08	27.0±0.5
8	16.9±0.3	27.8±0.4	21.8±0.4	5.7±0.1	0.68±0.08	27.2±0.7
9	21.6±0.4	26.8±0.5	20.8±0.4	7.5±0.2	1.5±0.1	21.7±0.8
10	23.2±0.4	25.6±0.4	18.2±0.4	8.6±0.2	0.5±0.1	24.0±0.7
11	23.8±0.4	25.1±0.4	16.3±0.4	7.7±0.1	0.35±0.08	26.7±0.7
12	23.2±0.4	22.2±0.4	16.0.2±0.4	9.0±0.1	*	29.6±0.7
13	25.7±0.3	23.0±0.2	17.3±0.3	8.8±0.1	1.3±0.1	23.8±0.5

*<0.3 wt%

Table 5. Results from XRF analyses of each composition following calcination at 1000 °C for 3h

	Chemical composition (Wt.%)										
	SiO ₂	Al ₂ O ₃	P ₂ O ₅	Na ₂ O	CaO	MgO	K ₂ O	Fe ₂ O ₃	TiO ₂	SO ₃	Cr ₂ O ₃
1	42.54	26.13	24.07	2.46	2.23	0.71	0.70	0.52	0.50	0.11	0.01
2	42.60	26.25	24.48	2.69	1.57	0.67	0.77	0.52	0.32	0.08	0.01
3	43.41	26.01	26.12	0.98	1.63	0.03	0.71	0.52	0.36	-	0.01
4	41.44	26.27	25.26	2.31	2.33	0.67	0.77	0.52	0.31	0.09	0.01
5	48.17	30.50	15.83	1.54	1.39	0.65	0.83	0.60	0.37	0.1	0.01
6	48.36	29.88	15.87	1.91	1.60	0.54	0.83	0.60	0.37	0.02	0.01
7	48.06	29.85	15.49	1.80	1.85	0.71	0.77	0.59	0.52	0.05	0.01
8	47.43	28.99	15.85	2.87	2.30	0.71	0.85	0.57	0.41	-	0.01
9	45.36	28.38	18.66	2.53	2.58	0.70	0.85	0.56	0.34	-	0.01
10	45.17	28.28	19.17	3.16	1.89	0.61	0.85	0.57	0.34	-	0.01
11	45.90	27.87	19.22	2.77	1.79	0.56	0.78	0.57	0.54	-	0.01
12	45.99	28.44	19.00	2.57	1.62	0.61	0.82	0.58	0.40	-	0.01
13	45.42	28.50	19.27	2.06	2.30	0.70	0.80	0.57	0.35	-	0.01

FIGURE CAPTIONS

Fig.1. XRD patterns for metakaolin used as raw material for sample preparation (a) as well as the natural limestone used as pore forming agent (b).

Fig. 2. Low-magnification BSE images of polished cross-sections of samples having compositions 10 (a) and 3 (b).

Fig. 3. The Rietveld refinement output of an as-prepared sample having composition 3. The observed, calculated and difference curve are depicted. The tickmarks indicate the following phases starting from the top: quartz, muscovite/illite, tridymite, corundum (NIST 676a).

Fig. 4. The results obtained for various properties of the heat-treated foams as a function of the corresponding values obtained for as-prepared samples: (a) true density ρ_t , (b) bulk density ρ , (c) Total porosity TP, (d) Thermal conductivity TC.

Fig. 5. $dV/d\log D$ (V =volume of intruded mercury) and the cumulative pore volume (indicated by arrows) as a function of pore diameter (D) for specimens with sample compositions 3 (a) and 10 (b). Data for both as-prepared (continuous line) and calcined (1000°C, dotted line) samples are depicted.

Fig. 6. Results of the thermogravimetric analysis of a powder obtained from a sample having composition 3.

Fig. 7. *in-situ* XRPD data (650-960 °C) collected for a sample having composition 3. The insert shows the FQPA results in which the known amount of intrinsic quartz was used as internal standard.

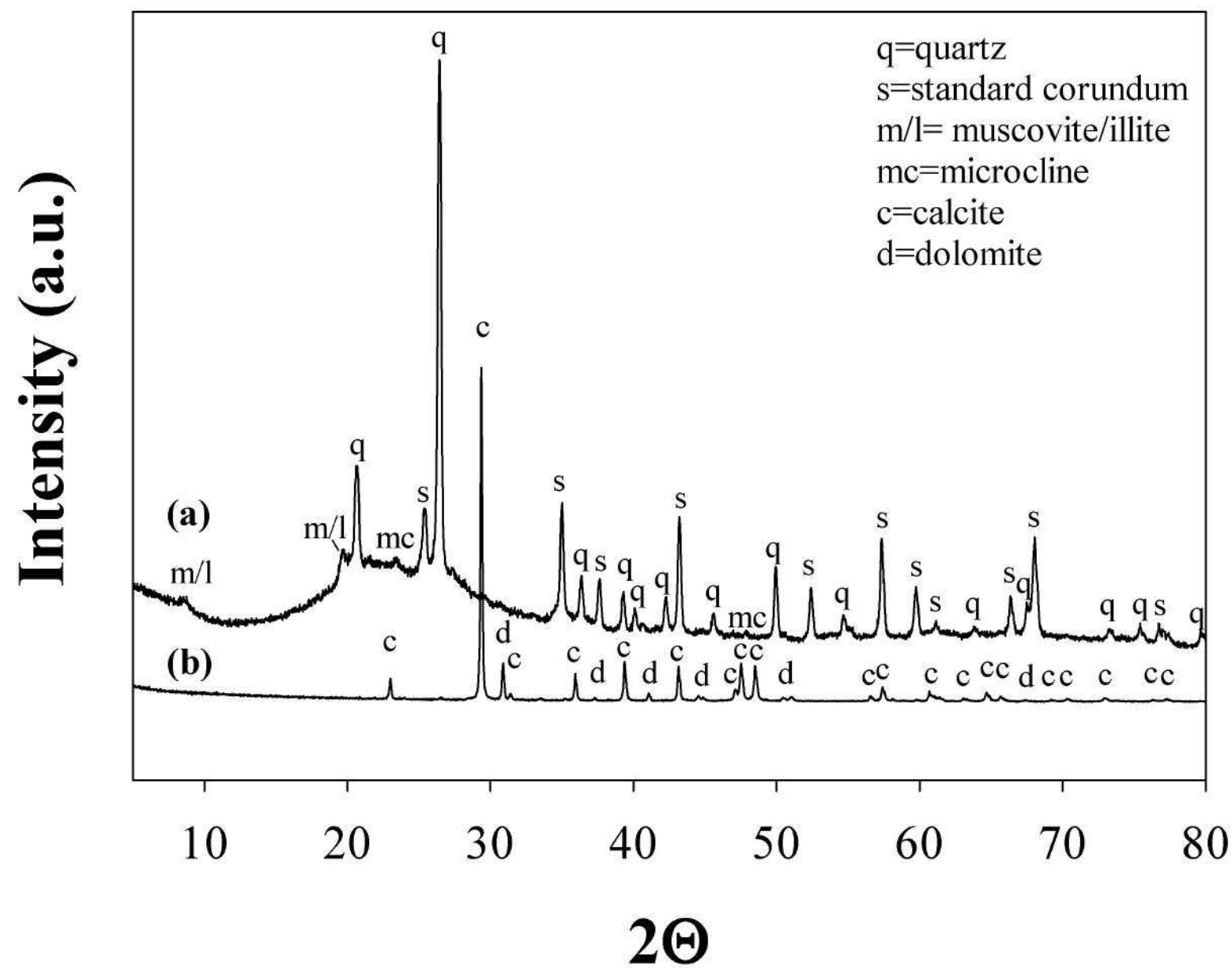
Fig. 8. XRPD patterns for specimens obtained by calcination of a sample having composition 3. The duration of the heat-treatment was 3h and the investigated temperatures were 800, 900 and 1000 °C.

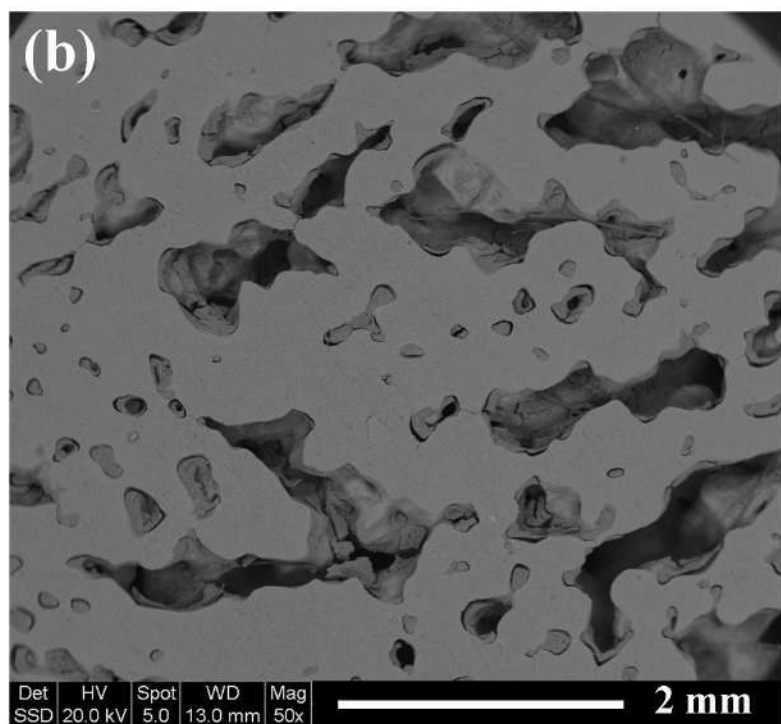
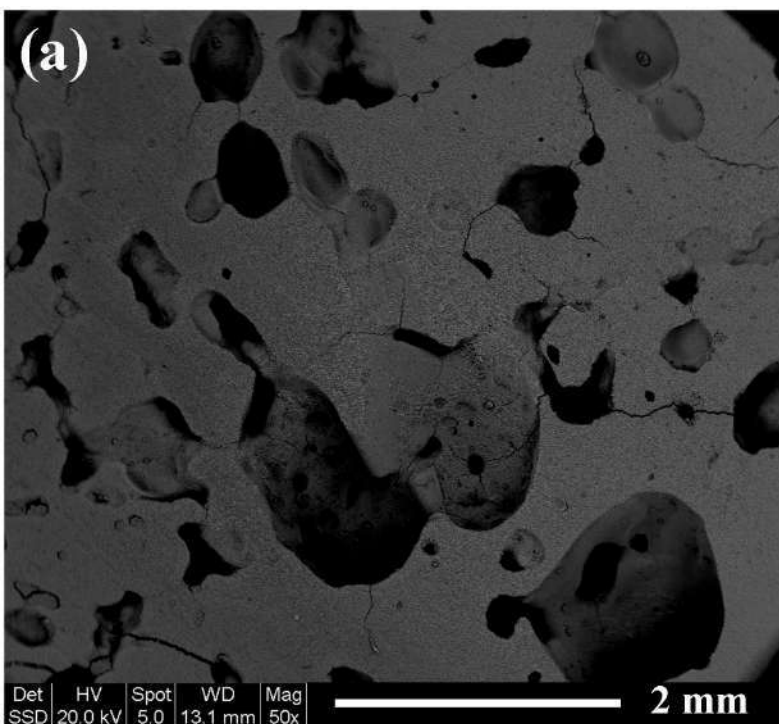
Fig. 9. Wt.% of major phases as a function of calcination temperature for composition 3.

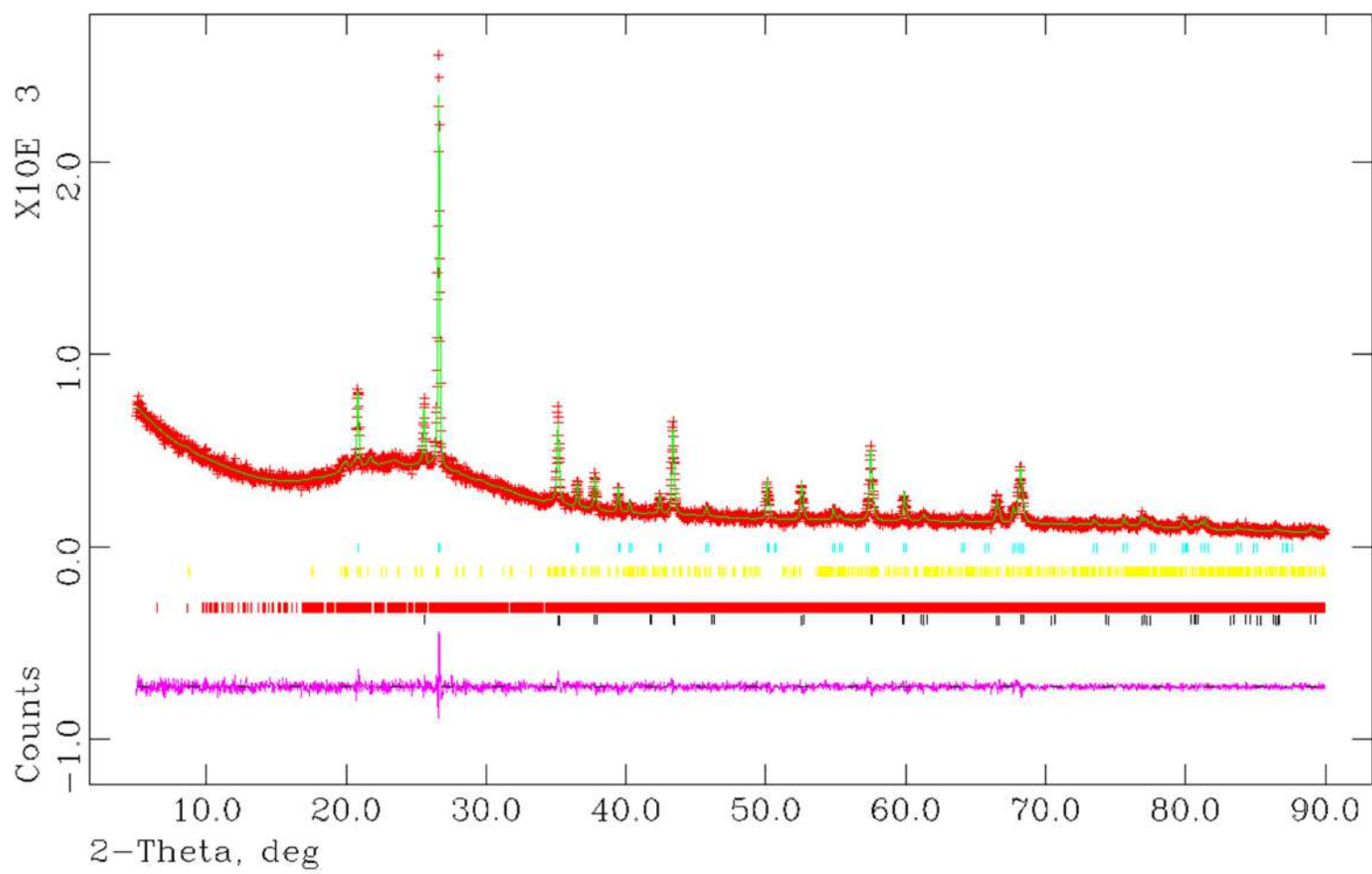
Fig. 10. TEM images of a calcined (1000°C) specimen having composition 3. Results from EDS spot analyses (molar composition, oxygen excluded) are reported. See text for definition of symbols (A,B,C,D).

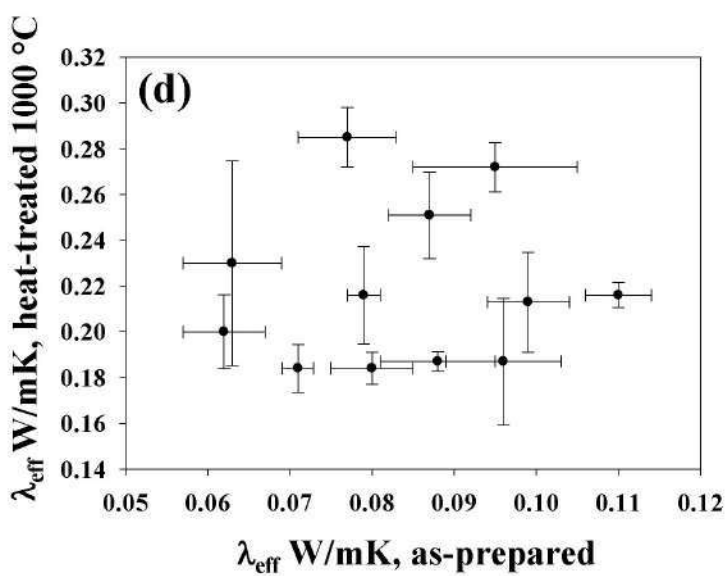
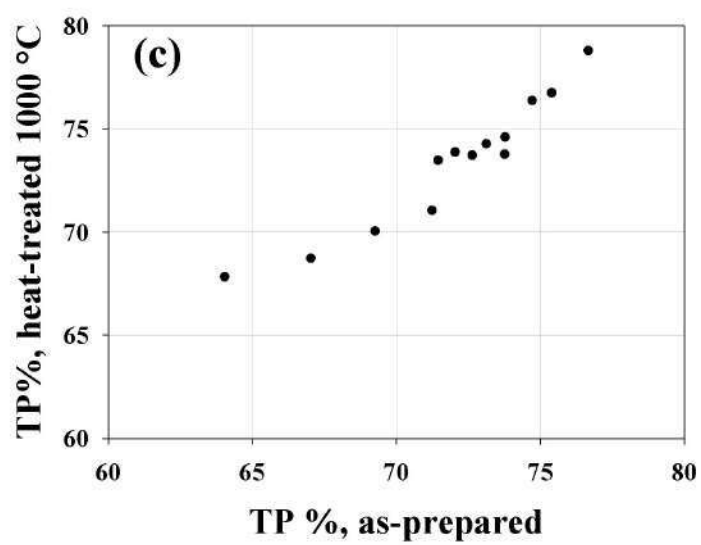
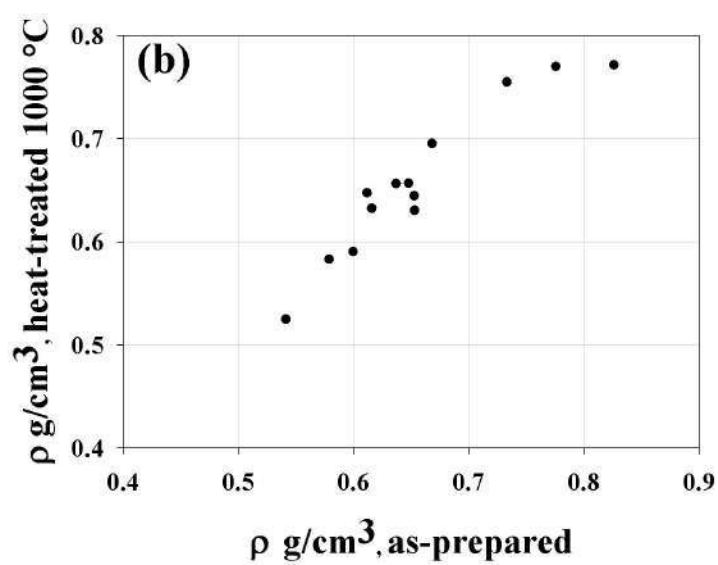
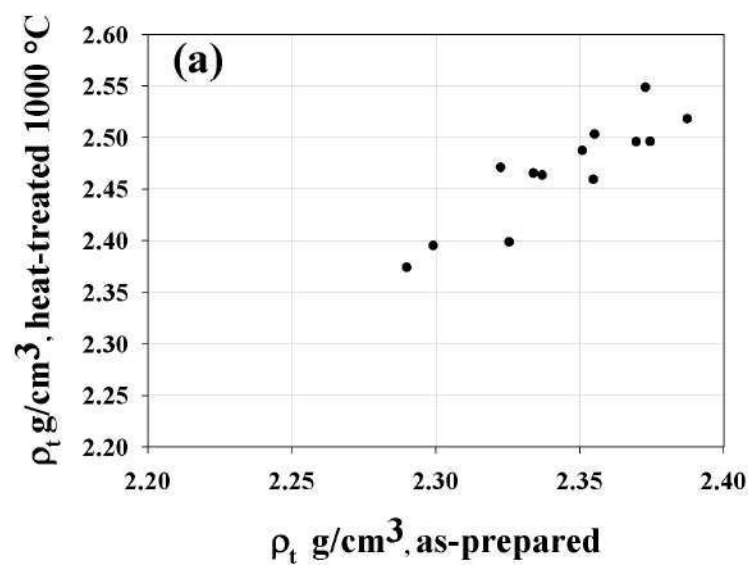
Fig. 11a. Unit cell volume of cristobalite as a function of temperature (*in situ* data) for a sample (composition 3) precalcined at 800 °C and 1000 °C. Literature data for AlPO_4 - SiO_2 and SiO_2 - AlPO_4 cristobalite solid solutions are also shown for comparison.

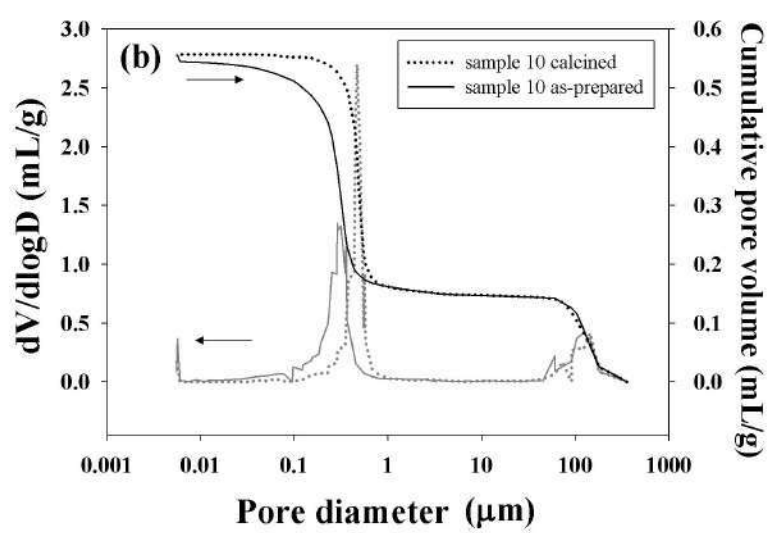
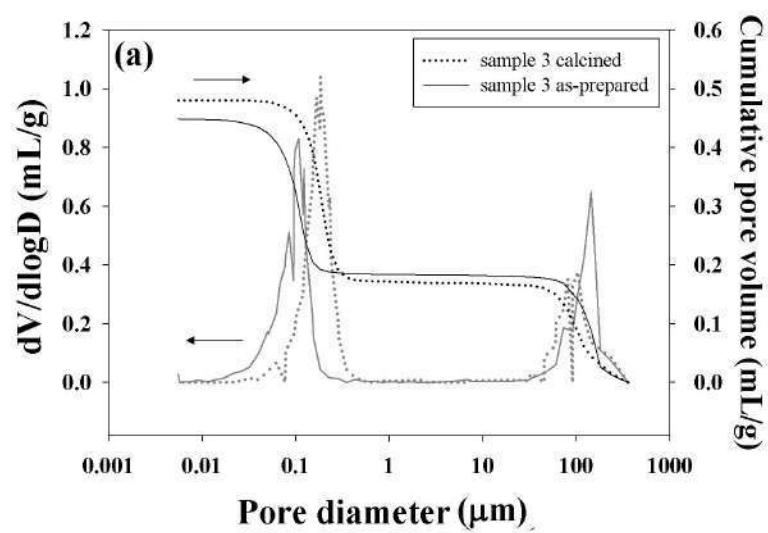
Fig. 11b. Unit cell volume of tridymite (triclinic, space group *F1* [31]) and quartz as a function of temperature (*in situ* data) for a sample (composition 3) precalcined at 800 °C and 1000 °C.

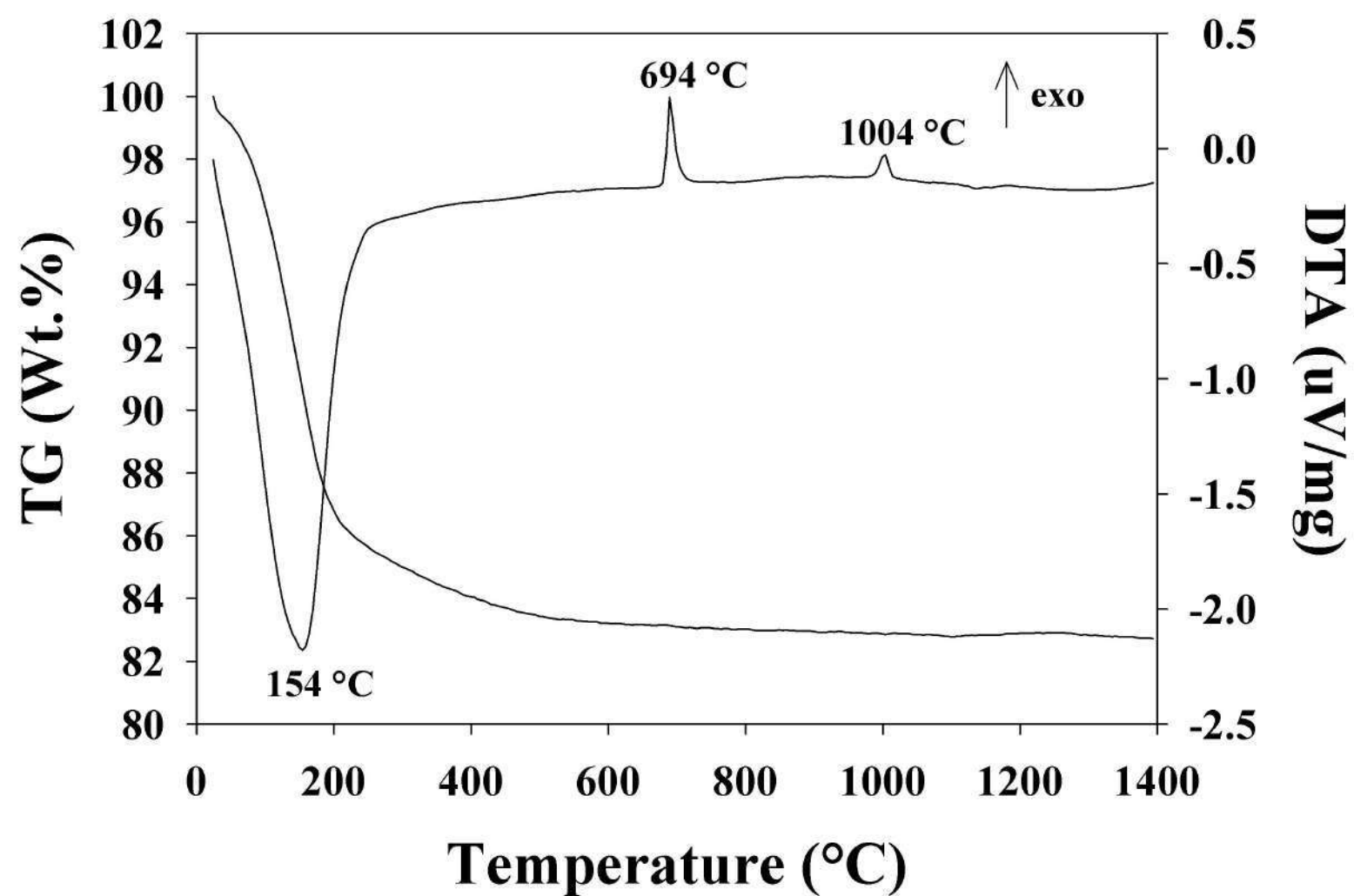


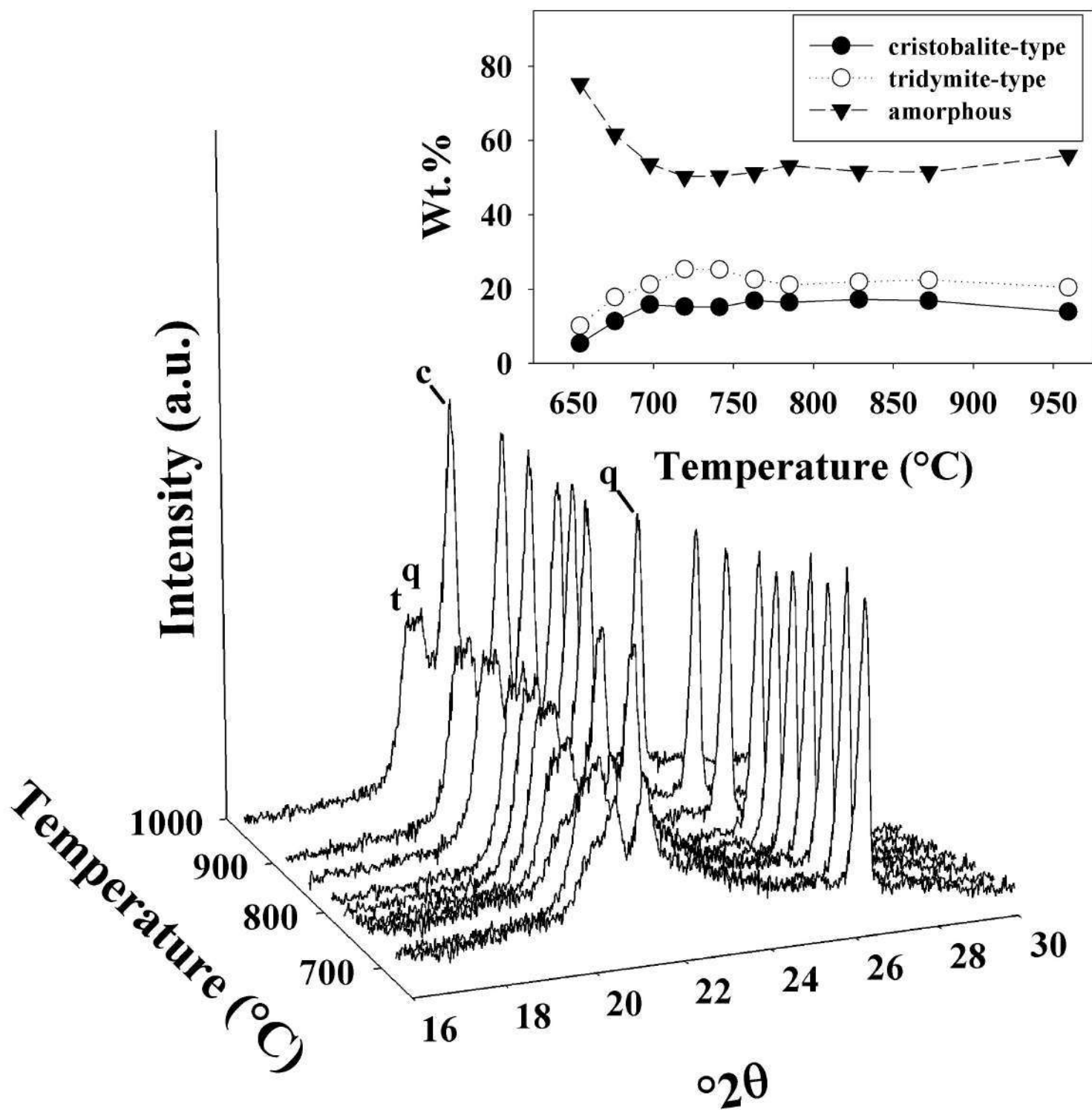












Intensity (a.u.)

