Optical Transmittance Changes of Solid Preforms with Temperature I. High Pressure Densified Hydroxyapatite Gels

[a]R. ĎUROVČÍKOVÁ, [b]V. KREMNIČAN, [c]Š. KOVALÍK, [a]Š. SVETÍK, [d]J. KRIŠTÍN, [e]P. M. MARQUIS, and [a]J. MAJLING

[a]*Department of Ceramics, Glass, and Cement, Faculty of Chemical Technology, Slovak University of Technology, SK-812 37 Bratislava*

[b]*Data System Laboratory, Ltd., SK-821 08 Bratislava*

[c]*Department of Materials Science and Technologies, Faculty of Mechanical Engineering, Slovak University of Technology, SK-831 02 Bratislava*

[d]*Central Laboratory of Electron-Optical Methods, Comenius University, SK-842 12 Bratislava*

[e]*School of Dentistry, The University of Birmingham, Birmingham B4 6NN, United Kingdom*

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The light transmittance—temperature patterns are recorded and partially interpreted for thin pellets of hydroxyapatite gels consolidated by the cold isostatic pressure (500 MPa and 1000 MPa). In the course of processing the precipitated wet gels were washed by methanol, ethanol, and propanol, prior to their drying and a subsequent high pressure consolidation.

Three important processes taking place have been identified by means of these patterns: the elementary carbon evolution and its subsequent oxidation at temperatures around 600 °C, the shrinkage of samples in the temperature interval between 700 °C and 1000 °C, and also a bloating of samples at temperatures above 1000 °C.

The one-line measurements of the optical transmittance of solids, especially at high temperatures, are not much pursued, chiefly because of the intense ("unpleasant") background radiation of furnaces, being the unavoidable parts of the pertinent devices.

Respectively, the information on measurement of the temperature dependence of the optical transmittance at temperatures above *ca.* 600 °C is missing from the literature. The temperature interval up to *ca.* 600 °C is, however, an operating range for some commercial hot-stage microscopes (FP84HT of Mettler Toledo, or KSPS 1000 of A. Krüss Optronic).

In our previous paper [1] we have established the principal accomplishment of such measurements, investigating sintering of thin hydroxyapatite plates. Recently, applying a more advanced experimental technique, we have brought further evidence on possibilities of this thermo-optical method to investigate not only the sintering phenomena, but also some other special occurrences in the microstucture of a thermally treated material.

Present measurements are carried out to see the influence of certain processing parameters upon the character of the transmittance recordings (washing of hydroxyapatite powders in a low surface tension polar liquids [2, 3] and their high pressure consolidation – 500 MPa and 1000 MPa).

The recorded "spectra" are compared to dilatometric measurements. The results are quite novel, so the primary intention of this work is just to point out to some characteristic features of obtained recordings at which the interpretation of the associated transmittance changes is more or less straightforward. The detailed interpretation of these recordings (sometimes called spectra) is a matter of future work.

EXPERIMENTAL

The hydroxyapatite gel was prepared by its precipitation from $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ solutions, using chemicals of reagent quality, with pH of solutions adjusted to 11.5 and $n(Ca)/n(P)$ ratio pre-set to 1.8. The precipitation was accomplished by simultaneous pouring 0.5 M solutions into the vessel of a mixer operated at a high revolving speed. The obtained gel was decanted several times (until pH = 7). It was finally filtered on a Büchner funnel and redispersed from a wet state into either methanol, ethanol, or propanol.

The filtration and redispersion in the respective alcohols was repeated twice. The wet filter cakes were subsequently dried in a microwave oven. The dry or seemingly dry gels were pressed in a cylindrical steel die (ø = 12 mm) to discs approx. 1 mm high at a pressure 50 MPa. When the gel was liquefied under the applied pressure, its drying in microwaves was continued. The received discs were positioned between PE foils which were thermo-welded yielding discs encapsulation. The PE capsules thus received were vacuumed to some extent by an extraction of the air by means of a syringe and needle. The final isostatic pressing was accomplished at either 500 MPa or 1000 MPa. The densities of samples were measured from their mass and geometrical dimensions.

The light transmittance—temperature spectra were measured using the device of DSL, Ltd., Bratislava, operating up to 1300 °C.

The hydroxyapatite pellets were irradiated to their upper side by focused light from a high efficiency LED (light emitting diode). The transmitted light was collected by an objective and fed to a sensitive Si photodiode. The temperature control, data acquisition, and storing of the measured transmittance was made by an icon-based software which runs under WINDOWS on a PC. All experiments were performed at a heating rate of 10 °C min^{-1}. Sample temperature was measured by the PtRh10/Pt thermocouple.

The presence of elementary carbon was identified by the Electron Microanalyzer JXA 840 (Jeol). XRD analysis was performed by DRON 2 powder diffractometer (Cu$K\alpha$ rad.). Dilatometric measurements were performed using 402 E Netzch equipment.

Table 1. Relative Green (G.D.) and Final (F.D.) Densities of Samples Pressed to 500 MPa

Sample	G.D.	F.D.
5 MET 1*	0.614	0.852
5 ET 1	0.585	0.815
5 ET 2	0.597	0.899
5 ET 3	0.597	0.869
5 PROP 1	0.563	0.855
5 PROP 2	0.548	1.0
5 PROP 3		1.0

*Sample washed in methanol easily fragmented after pressing.

RESULTS AND DISCUSSION

The dry prepared hydroxyapatite gel, heated in a powder form to 1200 °C, was an X-ray phase pure product. Pressing of the dried gel to high pressures rendered glassy-like, fairly well transparent sample discs. When overlaid on printed text its characters were well discernible. Compacts washed in ethanol showed the faint yellow-greenish colour.

The green and the final relative densities of samples pressed at 500 MPa are given in Table 1, Figs. 1—3 show the transmittance changes with temperature. The highest measured bulk density (sample 5 PROP 2 – density 3.158 g cm^{-3}) was taken as a true density of hydroxyapatite. The effect is not a mere scaling of relative densities to the highest value observed, since the mentioned bulk density value measured is close to the one of the highest true density values (3.156 g cm^{-3}) reported for pure hydroxyapatite [4].

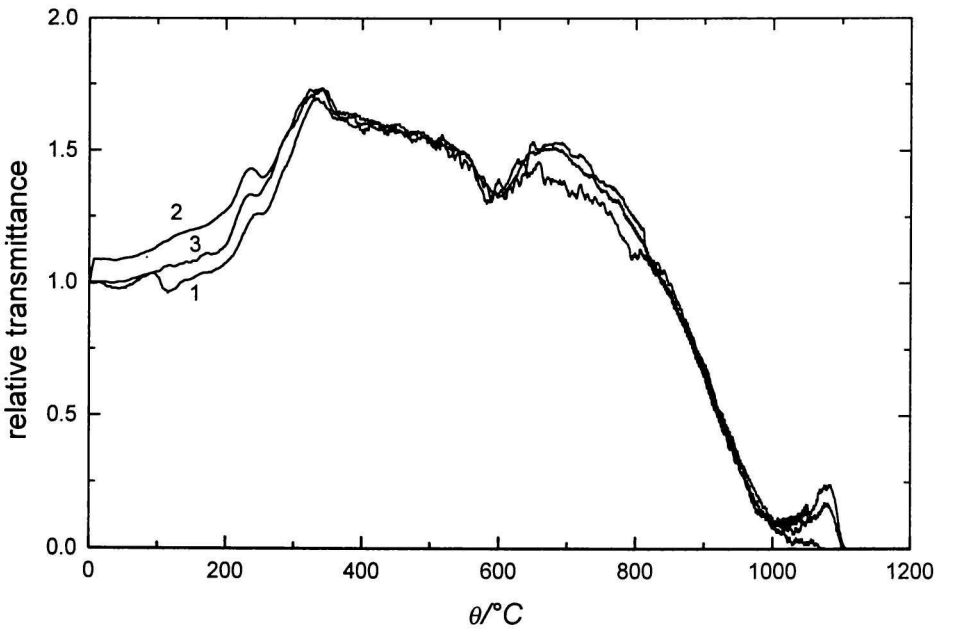

Fig. 1. Relative transmittance—temperature (TTS) spectra for samples washed in ethanol, pressed at 500 MPa (5 ET 1, 2, 3).

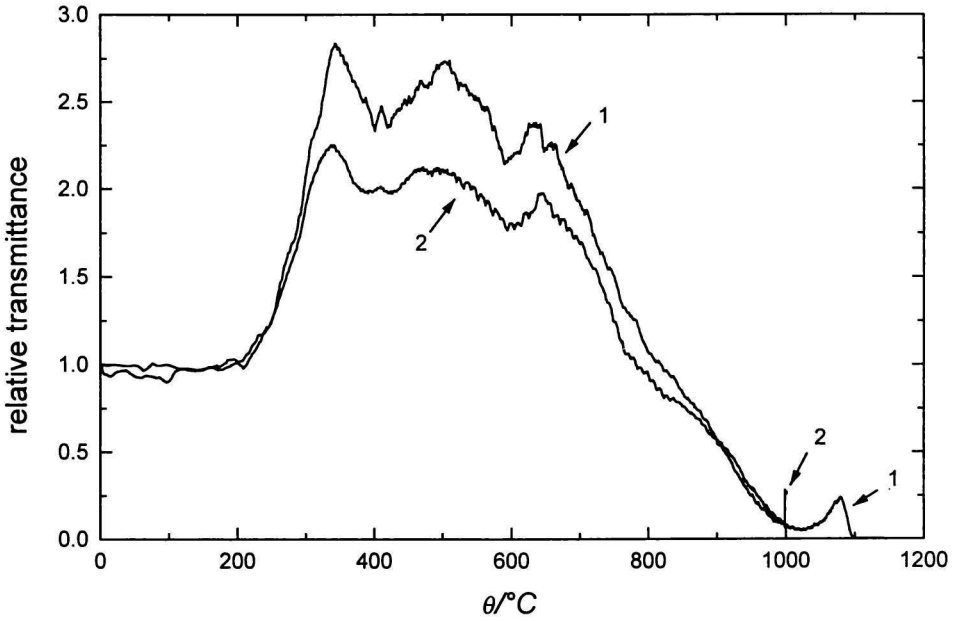

Fig. 2. TTS spectra for samples washed in propanol, pressed at 500 MPa (5 PROP 1, 2).

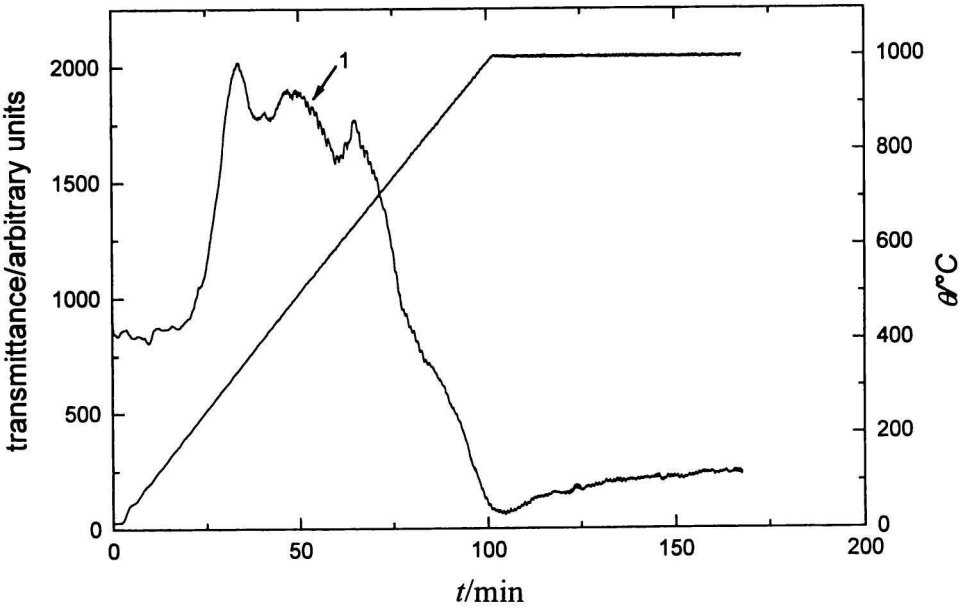

Fig. 3. TTS spectrum of the sample 5 PROP 2 (1), with included time—temperature profile.

To have an idea on reproducibility of measurements in recording the transmittances, in Fig. 3 three consecutive records are shown for samples prepared from gels washed in ethanol and pressed by 500 MPa. It is evident that the reproducibility of measurements is fairly good also on a level of some subtle transmittance changes. The patterns are drawn on a relative scale setting the initial values of the transmittances to 1. The reason is a better discrimination between a gain and a decrease in transmittances.

The spectra, in general, show an appreciable increase in transmittance inside the temperature interval from approx. 200 °C to approx. 400 °C. They also show the small decrease and a subsequent increase in the transmittance (local minimum in the transmittance) around the temperature of 600 °C. One of the characteristic features of spectra is also a continuous decrease in transmittance in the interval from 700 to 1000 °C and a tendency to recover the transmittance from its minimum value close above the temperature of 1000 °C. Next characteristic feature of the spectra is a sudden decrease in the transmittance to zero at temperatures above 1000 °C. Spectra of samples washed in propanol (Fig. 2) preserve a similar

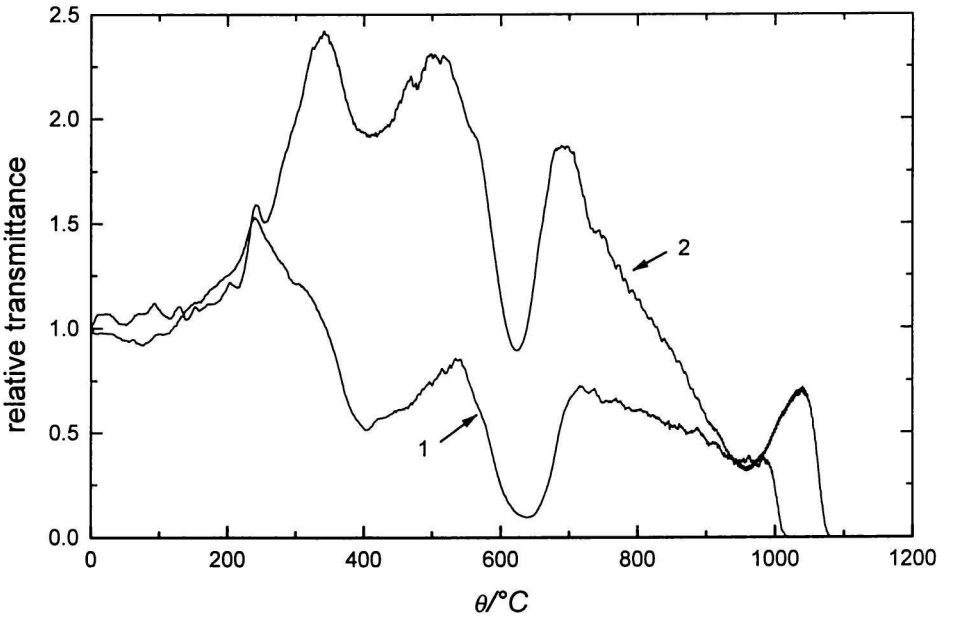

Fig. 4. TTS spectra for samples 10 PROP 1 and 10 PROP 2.

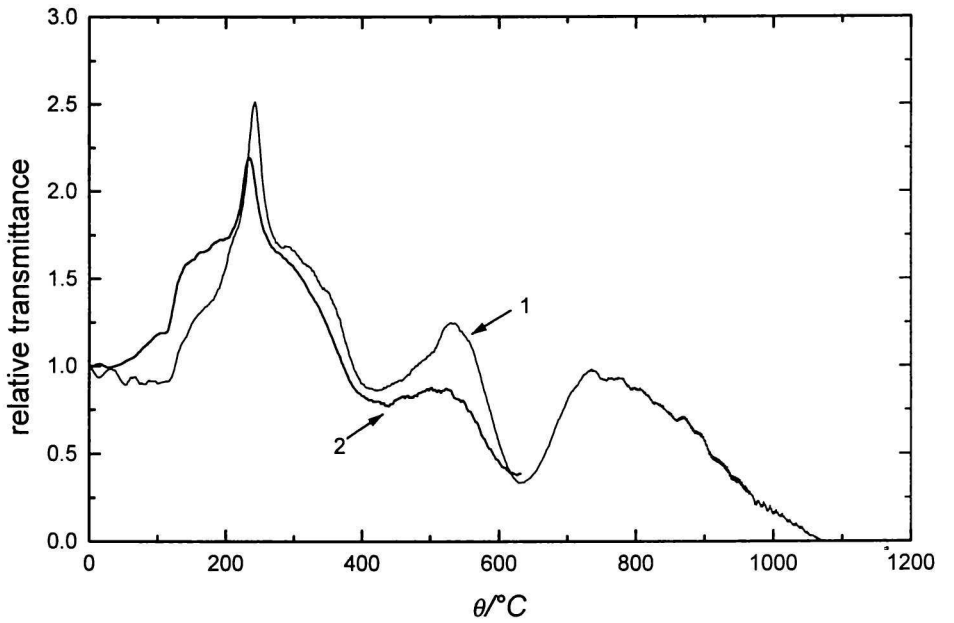

Fig. 5. TTS spectra for samples 10 MET 1 and 10 MET 2.

nature. The increase in transmittance at low temperatures is however more pronounced and, moreover, it is confined to the more narrow temperature interval. Also a small minimum in transmittance is observed at approx. 400 °C.

The reason for the sudden decrease in the transmittance of samples at 1100 °C is believed to be their bloating. Each sample showing such a drop in the transmittance was invariably opaque after its cooling to room temperature. Similar instability, consisting in bloating (expansion) of samples, was observed also elsewhere [5, 6].

In order to avoid bloating, the sample 5 PROP 3 was heated in a repeated experiment only to 1000 °C, with a soaking period of 75 min at this temperature (Fig. 3). The second curve of two linear parts shows the furnace temperature in a vicinity of the sample at its heating as well as at the corresponding isothermal run. At such a temperature schedule the sudden drop in the transmittance of the sample has been postponed and was actually not observed. The benefit of an avoidance of bloating is seen from Table 1 in which the relative densities of samples in the green state (after pressing) as well as after firing are given. The final

Table 2. Relative Green (G.D.) and Final (F.D.) Densities of Samples Pressed to 1000 MPa

Sample	G.D.	F.D.
10 MET 1	0.709	0.771
10 MET 2	0.429	0.473*
10 ET 1	0.572	0.535
10 ET 2	0.750	0.604
10 PROP 1	0.440	0.501
10 PROP 2	0.552	0.654

*Sample heated to 600 °C.

density of the sample 5 PROP 3 reached the highest density and was well translucent after the experiment.

The recorded spectra of samples pressed to 1000 MPa (Figs. 4 and 5) show a moderately different pattern compared to spectra of samples pressed to 500 MPa. There exists the closer similarity between samples processed with respective alcohols than between samples pressed at different pressures. Nevertheless, the transmittance minima at 400 °C and 600 °C, observed in previous cases, are repeated also at pressure of 1000 MPa, especially the minimum close to 600 °C is considerably deepened. The decrease in transmittance above 700 °C as well as the sudden drop in transmittance above 1000 °C is also observed.

Fig. 5 contains the spectra recorded for samples of 10 MET 2; one of them was only up to temperature 600 °C at which the furnace was switched off. The sample was wholly black after the experiment so it was presumed that the well resolved and broad peaks repeated in spectra with minima approx. at 600 °C belong to the evolution of carbonaceous species and an oxidation of the elementary carbon. Its presence is confirmed by the Electron Microanalyzer. The source of carbon is only tentatively discussed. One reason of its presence may be a cracking of the remnant organic molecules not removed completely by drying of powders and heating of pertinent pellets to *ca.* 600 °C. This effect seems to be less evident with compacts of less densely packed particles. Its second origin might be carbon dioxide decomposed to carbon at a surface of hydroxyapatite pellets similarly as it was found for certain active oxide phases (*e.g.* wustite) [7]. This cited reaction occurred, however, at temperature of 300 °C.

As it was mentioned all samples pressed to 1000 MPa were opaque and white in colour after their heating to 1200 °C, so all of them were expected to undergo bloating. Their bloating is evidenced also by the low final densities (Table 2).

In Table 2 only the samples 10 MET 1 and 10 ET 1 show such green densities as expected from the applied pressure level. The densities of other samples are unexpectedly low. There might be two reasons for this discrepancy. Either the densification was blocked above a certain pressure level by the presence of the remnant liquid in the gel pores, or the samples relaxed the pressure-induced strain by a kind of the sprig back effect. Such a relaxation, thermally induced however, was observed for instance in a case of the high-pressure alumina compacts [8]. The sharp increase in the transmittance in Fig. 5 at 250 °C remains unexplained.

Fig. 6 shows the dilatometric curves recorded for samples pressed at 500 MPa as well as for the samples pressed at 1000 MPa. The common feature of all dilatometric curves is their smooth S-shape profile at temperatures of sintering. The beginning of

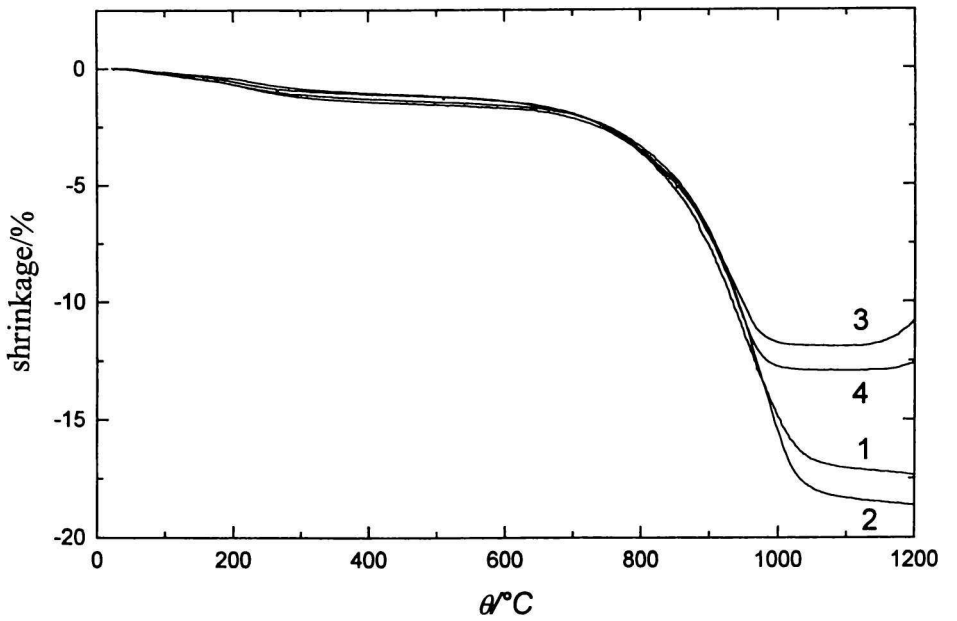

Fig. 6. Dilatometric measurements for samples 5 MET 1 (1), 5 PROP 1 (2), 10 MET 1 (3), and 10 PROP 1 (4).

sintering starts in all cases at the same temperature, what is well mimicked by a decrease of the transmittances. A similar case was observed in [1]. The sudden drops of the transmittance, most frequently observed at 1100 °C, cannot be matched to discontinuities on dilatometric curves. Unfortunately, dilatometric curves are taken only to temperatures of 1200 °C. Approaching however the temperature of 1200 °C there exists already a positive evidence for a beginning of the expansion of samples pressed at 1000 MPa. These measurements comply to ones cited previously [5, 6] at which the sudden expansion was also observed but at temperatures well beyond the temperatures at which the sintering was already finished. The sudden expansion of samples, as inferred from the decrease in the transmittance at *ca.* 1100 °C, needs to be confirmed by further measurements and supported by an investigation of corresponding microstructures.

The partial gain in the transmittances also remains temporarily unexplained, as *e.g.* seen from curve 1 in Fig. 2, or curve 2 in Fig. 4, at temperature close above 1000 °C. When interrupting the measurements at corresponding temperatures the samples are well transparent as it was evidenced in [9]. Local minima in transparencies prior to this gain may be interpreted also only with some caution. The dilatometric curves evidence at these temperatures the final stage of shrinkage. Their verification is a matter of further work.

CONCLUSION

The first-hand experience is mediated for a novel technique of the light transmittance measurements performed on hydroxyapatite pellets at linearly increased temperature. The measurements render a kind of spectra. Present evaluation of results points to some significant "qualitative" features of spectra, including their reproducibility. The consolidating pressure of the powder particles and the resulting difference in the green density of pellets as well as the used washing media cause an appreciable difference in the measured dependences. The relatively intense changes of the transmittance are encountered at low as well as at high temperatures. At low temperatures, the carbon evolution and its subsequent oxidation was observed, taking place in the powder pellets matrices at approx. 600 °C. At high temperatures the continuous decrease in the transmittance is associated with sintering process in correspondence with the results of dilatometric measurements. At the temperatures above 1100 °C the sudden drop in the transmittance is observed which is believed to be associated with swelling (sudden expansion) of samples. Further work is needed to explain the structure of spectra in more detail.

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