Design and application of a cost effective high temperature holder for *in-situ* powder X-ray diffraction experiments

L. Dimowa[1]*, B. Shivachev[1], S. Petrov[2]

[1] *Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences,*
"Acad. Georgi Bonchev" str. building 107, Sofia 1113, Bulgaria
[2] *Department of Chemistry, University of Toronto, 80 St. George Street,*
Toronto, ON, M5S 3H6 (Canada)

We are presenting a simple and inexpensive, in-home made high-temperature (HT) device, suitable for high-temperature *in situ* investigations of phase transitions, crystallite growth and other thermal features of solid-state materials by X-ray diffraction (XRD). The attachment can be easily mounted on conventional laboratory X-ray diffractometer. The HT-device consists of sample holder and heating element combined together. The unit is made from fused quartz, which temperature resistance is above 1000 °C. The sample holder (the front part of the body) can be shaped to match the conventional front packing powder holder for the equipment that is used. The heating element consists of a khantal tape that is mounted on the backside of the body. Different ways of mounting the heating tape can be used to optimize the desired uniform heat distribution within the volume of the packed powder. The length of the heating tape can be adjusted, for tuning its total resistance and accordingly – its heating power. Both the sample holder and the heating element are made "small" to ensure a good thermal exchange and to save energy required for heating. Due to its small size, limited contact with the diffractometer and the good thermal stability of quartz in air, the HT-device does not require water-cooling and can be used for multiple routine *in situ* measurements up to 950 °C. Its functionality was studied on standard reference material (KNO_3) and on natural minerals: a mixture of clinoptilolite/opal-cristobalite and Zn-exchanged clinoptilolite. The advantages and limitations of the proposed design are discussed.

Key words: high-temperature XRD holder, XRD, *in situ* heating.

INTRODUCTION

X-ray powder diffraction (XRPD) is one of the most recognized analytical tools for compositional and structural analysis of solid-state materials including various natural and synthetic technological products. The ongoing investigations on many of these materials required more complex and detailed information for their features, including thermal behavior. The HT-X-ray diffraction analysis, especially when carried out *in situ*, is capable to display instantly physical, chemical and structural changes that occur at certain temperature, but remain "hidden" at ambient conditions [1]. A variety of attachments (chambers, furnaces, cameras etc.) are commercially available for conducting such *in situ* experiments [2, 3].

DESIGN AND DISCUSSION

The holder is made of fused quartz as a replica of the original plastic/metallic sample holders used for our conventional Bragg-Brentano diffractometer, Dron 3.0 M (Fig. 1). The heating element is mounted on the opposite side of the sample holder. Some advantages of fused quartz include:

- Its thermal expansion is negligible (coefficient of $5.5 \times 10^{-7}/°C$ (20–320 °C),
- It is stable up to ~1100 °C (softening point is 1600 °C, annealing point is 1120 °C and strain point is 1025 °C),
- Multiple heating-cooling cycles can be carried out with temperature range up to 950 °C,
- It is inert (non-reactive) against very broad range of materials,
- When irradiated by X-rays fused quartz does not provide scattering or diffraction,
- Fused quartz is an insulator and cannot damage goniometer's base during the heating.

* To whom all correspondence should be sent:
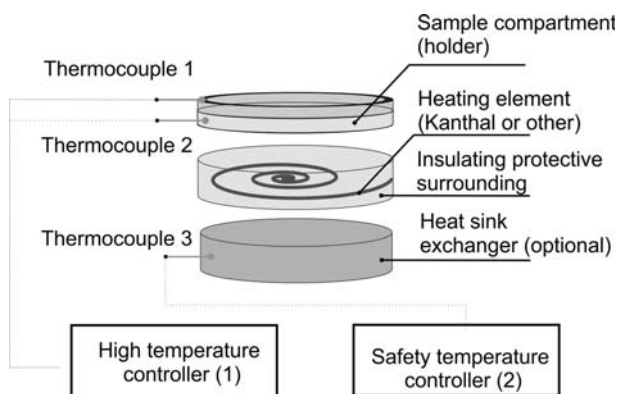E-mail: louiza.dimova@gmail.com

Fig. 1. Schematics of the high temperature holder

The body of the holder is made of cylindrical shaped piece of fused quartz with ø 25 mm, length 10 mm and consists of two parts:

1. Sample compartment (1 mm deep circle cavity with polished flat edges for precise alignment);

2. Heating element: in our case a kanthal tape, 1.5 mm width, 0.12 mm thickness;

The kanthal heating tape was inserted in thin-drilled channels on the backside of the sample compartment. Two modes of mounting the heating tape are possible: (1) – wire coiling and (2) – spiral coiling (Fig. 2). Wire coiling mounting of the heating tape has the advantage of allowing adjustments of its loops and distance between loops, which changes the total resistance of the tape and thus, its heating power. For fixed resistance parameters of the heating element, spiral coiling is the preferable option.

Two thin and flexible thermocouples (K-type) (~0.2 mm) are placed in different positions: (i) – inside the sample and near the diffracting surface and (ii) – closer to the heating element. Both of them are located on the border of the holder. They are used for control and adjustment of the temperature on the dif-
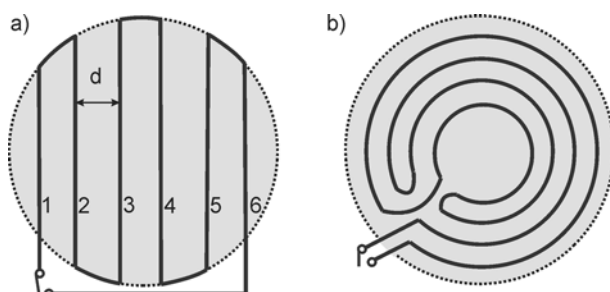

Fig. 2. Heating element placement: a) wire-coiling and b) spiral-coiling. The distance d between the channels could be adjusted by adding or subtracting turns, in order to obtain optimal total resistance and heating power

fraction surface of the sample. The use of two thermal elements helps for monitoring the thermal gradient and heat distribution in the volume of the sample holder.

The temperature is controlled by adjusting the current/voltage provided to the heating element as a function of the output of the two thermocouples. Optionally, a third thermocouple may be placed inside the capping of the heating element.

The holder is mounted directly on the diffractometer. A self-adjustment ("in plane") of the diffracting surface is ensured by three contact points (stoppers) mounted on the goniometer. As it was stated above, due to insignificant thermal transfer of fused quartz, the heat exchange with the contact stoppers and other goniometer's parts is limited.

SIMULATION OF THE XRD HOLDER

In order to understand the heat transfer in the entire holder, it was modeled and numerically simulated by finite element method (FEM) analysis using RadTherm 8. For the solid phases (fused quartz) heat conduction, surface-to-surface (in the sample holder) and surface to ambient radiation (outside) was applied. For the gas phase, the heat transmission and free convection were taken into consideration. Due to the presence of a heating element without clear symmetry, the holder was simulated in a three dimensional model (x-, y- and z-axes). For simplicity, a constant value for the heat conductivity of 3.8 W m^{-1} K^{-1} was assumed for the sample in all simulations. The simulation of the temperature distribution in the cell in ambient atmosphere and a heating power of $P = 85$ W is shown in Fig. 3. The temperature of the cooling air has been set to 20 °C. Ideally, the sample temperature should be homogeneous over the entire sample volume. As the sample is heated from the inside and cooled from the surface, we expect a temperature gradient within the sample, especially for samples with very low heat conductivity. The highest temperature gradient is in the middle of the sample along the z-direction (Fig. 3). Due to the axial symmetry (along z) the contribution to the total sample volume is higher at the border than in the middle. Thus, the diffraction contribution from the sample volume near the "border" is going to be higher than that one from the center. This justifies the location of the thermocouples near the border.

THERMAL BEHAVIOR AND CALIBRATION OF THE HOLDER

Experimentally the overall cooling effect of the air was determined by measuring the heating power, necessary to reach a certain temperature of the sam-
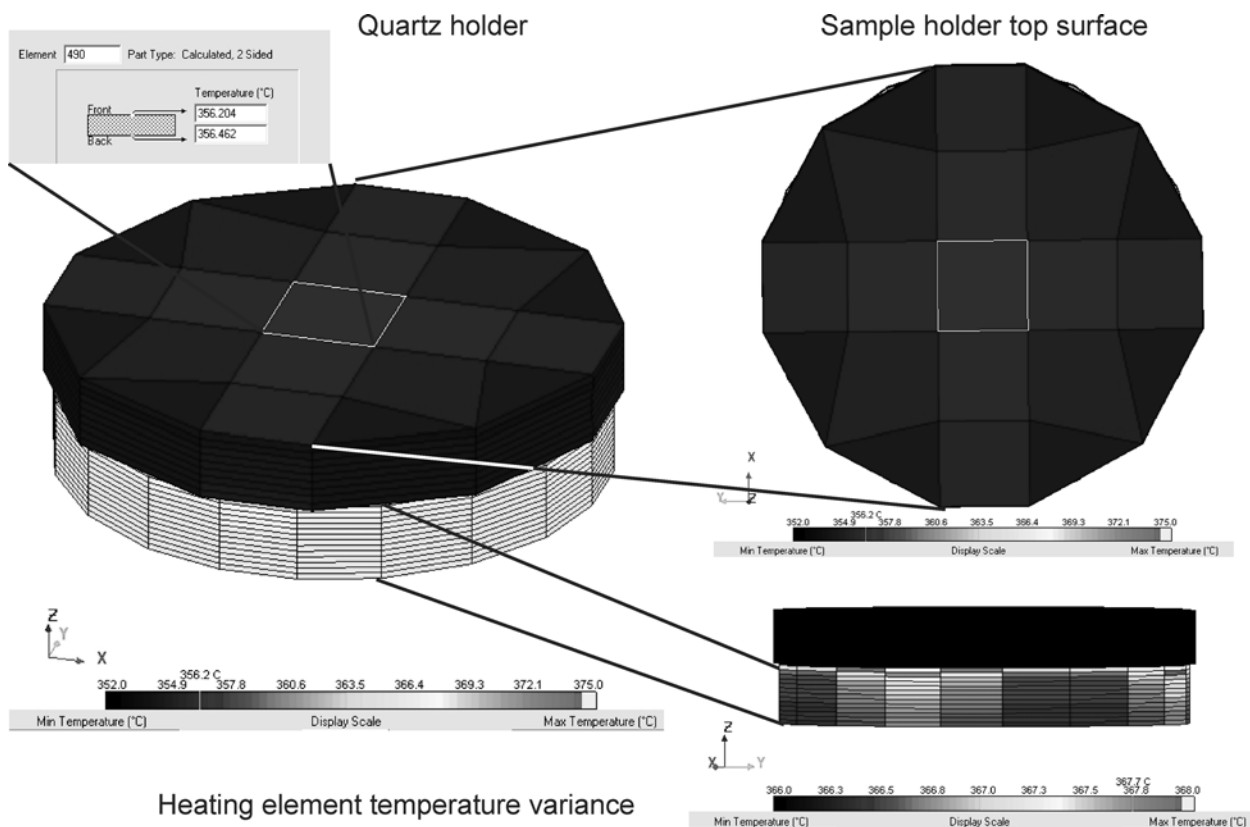
Fig. 3. Results from "finite element method" (FEM) simulation of the heat distribution in the sample holder in ambient atmosphere, heating power P = 85 W and temperature of the cooling air set at 20 °C

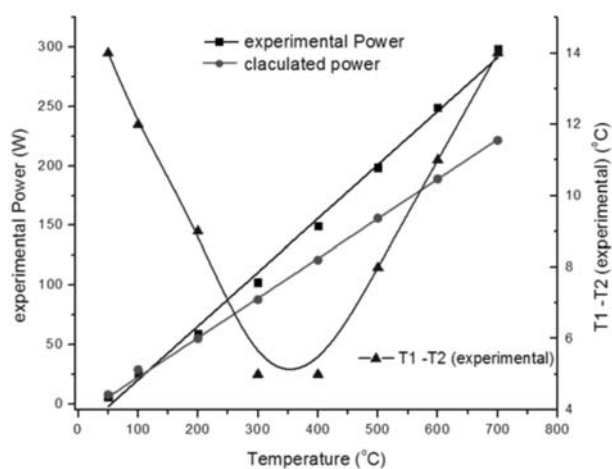ple holder. Figure 4 shows the applied "input power" as a function of the temperatures, measured by the two thermocouples: T1 and T2. The measurements were carried out after reaching and maintaining for 10 min the temperatures 50–100, 200, 300, 400, 500, 600 and 700 °C. The heating power as a function of sample holder temperature was found almost linear. The experimental temperature variation, T1 vs. T2, that corresponds to the thermal gradient within the volume of the sample was found smallest in the range of 250–400 °C and more pronounced at lower and higher temperatures. The simulated heating power values required for the holder to reach the requested temperature and the experimentally measured ones correlate well up to ~300 °C; beyond that temperature the real power input becomes significantly higher than the calculated one. This is probably due to the different heat capacity of the sample and the thermocouple as already observed by Kerestedjian & Sergeeva [4].

Fig. 4. Input power as a function of measured temperatures in the sample holder from the two thermocouples: T1 and T2

EXAMPLES OF APPLICATIONS OF HT-SAMPLE HOLDER

The holder was designed and mounted on a DRON 3M diffractometer (CoKα, 1.789 Å) equipped with position scintillation detector. The

system was interfaced with a personal computer. Data collection was carried out using a routine step scan mode with 0.02 or 0.04°.s⁻¹. Figure 5 shows the HT-sample holder as mounted on the goniometer and heated at 800 °C.

The holder has been tested against standard reference materials and used in our Lab for routine measurements on different materials [5, 6].

Here we are presenting the results from three HT *in situ* experiments carried out on different materials and at different temperature ranges.
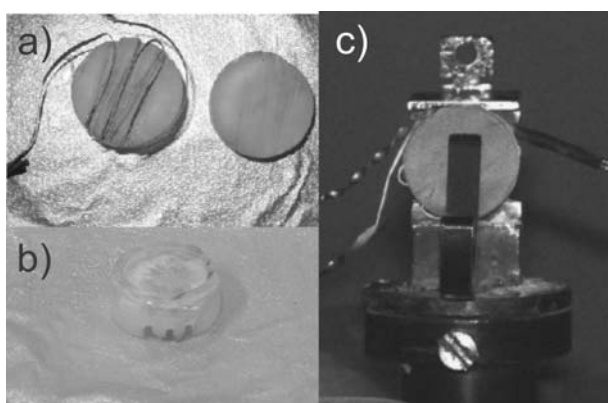

Fig. 6. In situ X-ray diffraction of reference material KNO₃: It shows a phase transition from orthorhombic (at room temperature) to rhomboherdal structure at 135 (±1) °C.

Fig. 5. View of: a) the heating element and its cover; b) the o-ring shaped sample compartment and c) the HT-holder mounted on a DRON 3M diffractometer and heated at 800 °C.

HT in situ experiment on reference material KNO₃

KNO₃ is known for having various polymorphous under certain thermodynamic conditions. Three of the polymorphs are stable at ambient pressure (7–10). At room temperature (RT) KNO₃ is orthorhombic, *Pnma*, with aragonite-type of structure (11). At temperatures above 129 °C it converts to calcite-type of structure $R\bar{3}m$, (8).

We used this material as a reference for testing the accuracy of our HT-sample holder. The observed structural transition of KNO₃ occurred at the same temperature as pointed out in the literature. This is illustrated on Figure 6, which displays the results from our *in situ* experiment carried out in routine step scan mode and elevating the temperature according to thermo couples showings with power control.
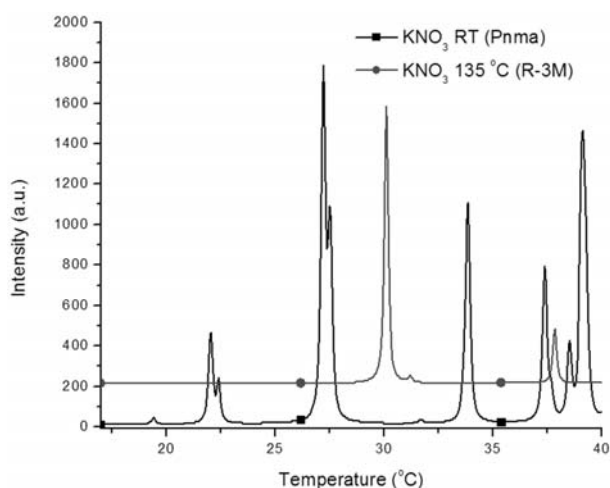
HT in situ experiment on natural mixture of clinoptilolite and opal-cristobalite

The natural zeolite mineral clinoptilolite from Beli Plast deposit, Bulgaria is commonly mixed with fine inter-grown sub-crystals of opal-cristobalite, having a visible peak on the diffraction pattern (d = 4.04 Å). It is well known that clinoptilolite undergoes lattice changes during heating, while opal-cristobalite has a stable structure that doesn't show lattice changes up to 1000 °C. A HT *in situ* experiment was done on this mixture in order to test and verify the overall alignment and possible positional displacements of the sample holder when heated. The heating was carried out up to 350 °C and the results are shown on Figure 7 – left plot. The position of the opal-cristobalite peak at *2θ* = 25° is marked with black arrow. It does not move during the heating. In contrast, the strongest peak of clinoptilolite next to it (marked with red arrow) moves due to its well established lattice changes when heated.

HT in situ experiment Zn-exchanged clinoptilolite

Our previous investigation on the thermal stability of natural clinoptilolite with various cations incorporated in its framework shows their different thermal stability. Here we demonstrate the collapse of the structure at temperature above 700 °C (Figure 7 – right plot). The experiment was carried
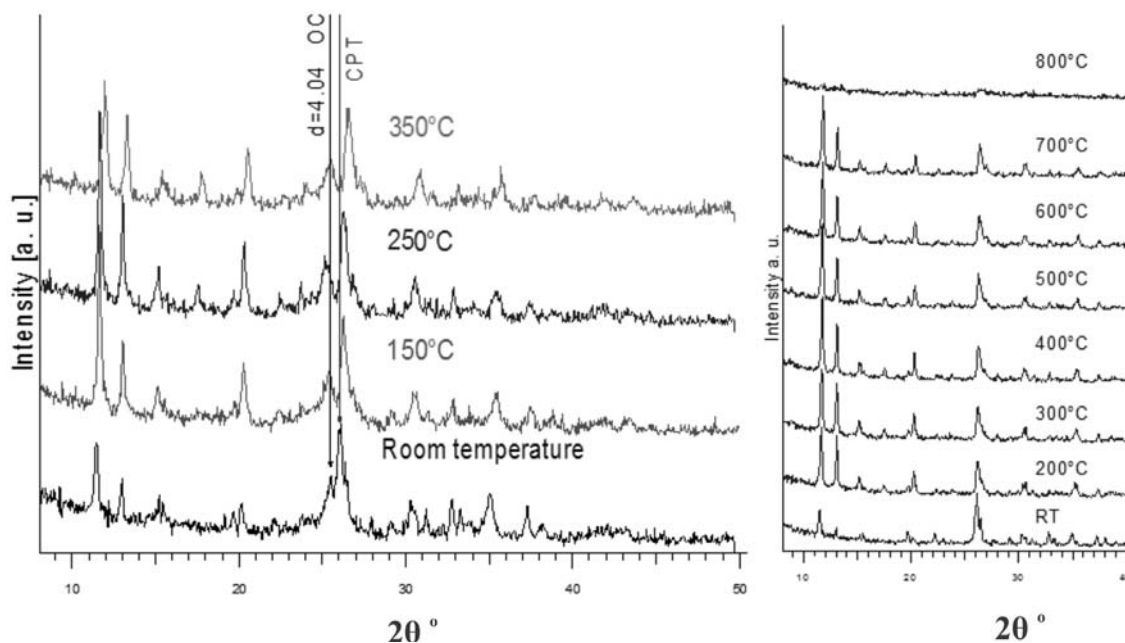
Fig. 7. Monitoring of CPT/Opal unit cells changes on heating (left plot) and thermal stability of Zn-exchanged natural clinoptilolite in the temperature range from RT to 700 °C (right plot)

out with our HT-sample holder and illustrates well its capabilities to be used for high-temperatures (up to 900–950 °C).

CONCLUSIONS

The design and construction of our "in home" HT-device, including sample holder and heating element are presented and explained in details. The design and setup were simulated and optimized by FEM analysis. The temperature can be properly controlled by two separate thermocouples and adjusted by power supply on the heating element. Due to the good thermal stability and negligible thermal expansion coefficient of fused quartz, the device can be used for multiple cycles of *in situ* heating/cooling in the temperature range from RT up to 900 °C. The accuracy of the alignment and its reliability has been tested and demonstrated here on three examples of HT *in situ* measurements on: reference material (KNO_3), natural mixture of clinoptilolite and opal-cristobalite and Zn-exchanged clinoptilolite.

The device is non-expensive, easy to be made and can be adapted and used on most of the conventional Bragg-Brenatano diffractometers.

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ДИЗАЙН И ПРИЛОЖЕНИЕ НА ЛЕСНА ЗА НАПРАВА ВИСОКОТЕМПЕРАТУРНА ПРИСТАВКА ПОДХОДЯЩА ЗА *IN-SITU* ПРАХОВИ РЕНТГЕНО ДИФРАКЦИОНИ ИЗСЛЕДВАНИЯ

Л. Т. Димова[1]*, С. Л. Петров[2], Б. Л. Шивачев[1]

[1] Институт по Минералогия и кристалография, БАН, ул. „Акад. Георги Бончев“, бл. 107, София 1113, България
[2] Университет в Торонто, Химически факултет, ул. „Сейнт Джордж“ 80, Торонто ON, M5S 3H6 Канада

(Резюме)

Представена е схема на високо температурна приставка (ВТП) подходяща за монтиране на прахов рентгенов дифрактометър и провеждане на *in situ* изследвания на свързани с фазови преходи, кристален растеж и други температурно зависими характеристики на твърдотелни материали. Приставката е сравнително лесна за направа и може да бъде монтирана на стандартен лабораторен рентгенов дифрактометър. ВТП се състои от два основни елемента: поставка за образеца и нагряващ елемент. Поставката е изработена от кварц с температура на топене над 1000 °C. Предната (фронталната част) на поставката трябва да е оформена така че да съответства на стандартния отражателен модел на съответния дифрактометър. Нагряващите елементи са от Кантал (ленти) които са прикрепени към задната част на поставката. За оптимизиране на равномерното разпределяне на температурата в обема на поставения прахов материал могат да се използват различни начини за монтиране на нагряващите елементи. Дължината на нагряващия елемент (съответно неговото съпротивление) може също да варира, което позволява по-точно нагласяне на мощността на нагряване. Размерите на приставката са минимизирани с оглед осигуряване на минимален температурен обмен с околната среда и консервиране на енергията. Поради малкия размер, ограничения контакт с дифрактометъра, добрата термична стабилност на кварца на въздух (до 950 °C при атмосферни условия) ВТП не изисква водно охлаждане и може да се използва многократно при рутинни *in situ* измервания. Функционалността на приставката е изпробвана върху стандартен еталонен материал (KNO_3) както и при *in situ* нагряване на природен клиноптилолит примесен с опал-кристобалит и клиноптилолит обменен с цинк. Представено е кратко разглеждане на предимствата и ограниченията на предложения дизайн и модел на ВТП.