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A HEATER ATTACHMENT TO HZG-4 X-RAY DIFFRACTOMETER

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A simple and inexpensive heater attachment to the HZG-4 X-ray diffractometer, which can be used for investigation of thermal behavior of solids between 20 and 300 °C, is described. Using of this attachment is documented on a study of dehydration of $[Mn(H_2O)]_{0.25}(VO)_{0.75}PO_4.2H_2O$ *and intercalation of ethanol into* $VOPO_4$.

Introduction

Commercial heater attachments to X-ray diffractometers are very expensive and often such complex and expensive units are not necessary, especially when the temperature range is not too large. In addition, for the diffractometer HZG-4 (manufactured by VEB Freiberger Präzisionsmechanik, GDR) no heater attachment is available. Ease of fabrication in any small workshop and no disturbance to the geometry of the X-ray diffractometer set up were two important conditions in the design and fabrication of this heater attachment. In our laboratory, we successfully fabricated and used a very simple heater attachment, which is able to work up to 300 °C. Construction details and some examples of utilization of this attachment are described in this paper.

Description of the Heater Attachment

Figure 1 shows total view of the heater attachment. This apparatus is composed of a duralumin frame (A), to which 1 mm thick corundum plate (B) is fixed by four metal clamps. Teflon foil of 0.1 mm thickness is used to diminish heat transfer from the corundum plate to the duralumin frame which holds the heater attachment in the diffractometer. Heating coils (H) are placed in two couples of holes in the corundum plate. A Ni-NiCr termocouple is attached at the opposite side of the corundum plate between the coils. Outputs of the thermocouple are fixed on the sides of the duralumin frame (T) in the same way as inputs of heating coils (P). The total dimensions of this heater unit are: 35 mm width, 70 mm length, 9 mm thickness. The sample (S) is placed in the space between the heating coils as a thin powder layer. This heater attachment allows measurements from the starting angle of 2°(2θ).

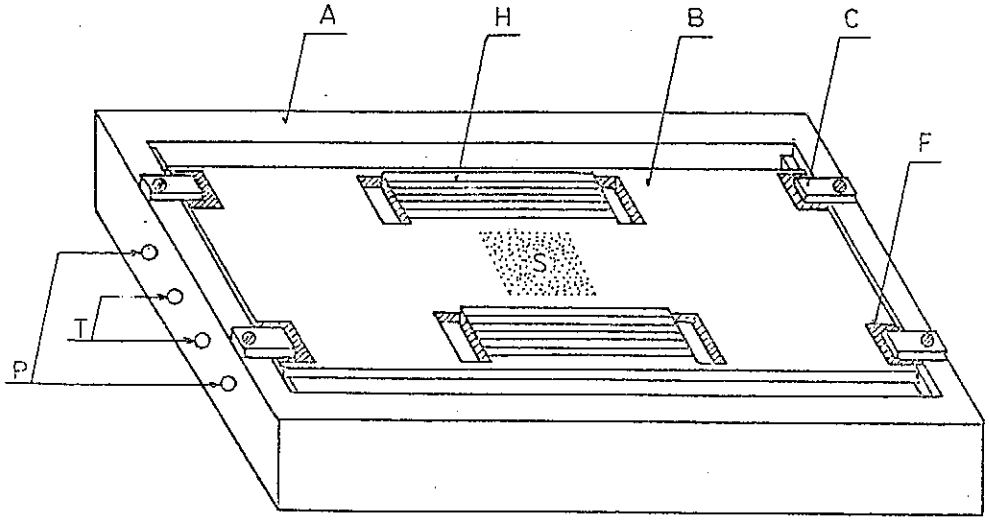

Fig. 1 Heater attachment for X-ray diffractometr.

A low-voltage source is used for the heating of the attachment, which allows to keep temperature as stable as ±2 °C. The heater unit was fixed to the sample holder of the goniometer and even after several hours at temperature about 300 °C, the sample holder of the goniometer did not get heated above 35 °C. The construction of the heater attachment does not allow to work at temperatures above 300 °C, because paste used for bonding the thermocouple to the corundum plate can be destroyed.

Examples of Measurement

Dehydration of vanadyl phosphate dihydrate was studied by means of the above-described apparatus[1]. The diffractograms of the compound with formula $[Mn(H_2O)]_{0.25}(VO)_{0.75}PO_4.2H_2O$ (Ref.[2]) in the temperature region from 22 to 212 °C are given in Fig. 2. It is obvious from these diffractograms that the primary dihydrate loses one molecule of water at about 50 °C and the monohydrate formed changes to anhydrous compound $[Mn(H_2O)]_{0.25}(VO)_{0.75}PO_4$ at a temperature above 110 °C.

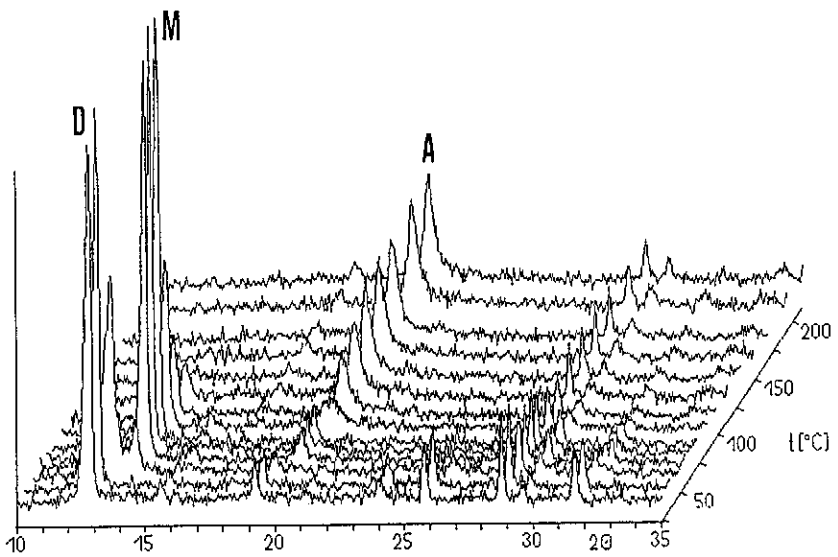

Fig. 2 Temperature dependence of diffractograms (CuKα radiation) of $[Mn(H_2O)]_{0.25}(VO)_{0.75}PO_4.2H_2O$. Temperatures of the measurement were 22, 32, 43, 61, 69, 82, 94, 110, 127, 145, 163, 190 and 212 °C. The (001) lines are marked D for dihydrate, M for monohydrate and A for anhydrous compound

With the heater attachment, it is possible to observe also a course of intercalation reaction by preparing anhydrous $VOPO_4$, which is very sensitive to air humidity, directly in the diffractometer without any additional manipulation. The anhydrous host was prepared by heating the $VOPO_4.2H_2O$ to 250 °C for 1 hour, followed by cooling to ambient temperature in a stream of dry air (0.5l/min). Dry air was blown to the sample from the 2 cm distance. The intercalation of water into vanadyl phosphate was studied and a formation of the Hendricks-Teller disordered layered structure based on a random stacking of $VOPO_4.2H_2O$ and $VOPO_4$ was observed[3]. The diffractograms depicting a time course of intercalation of ethanol into anhydrous vanadyl phosphate are shown in Fig. 3. A gradual decrease of intensity of the (001) line of anhydrous

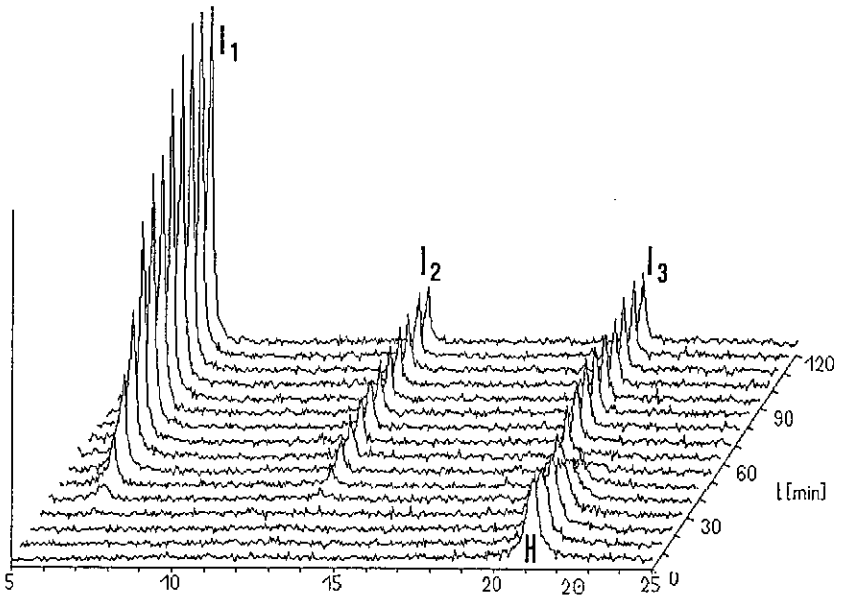

Fig. 3 Time dependence of diffractograms (CuKα radiation) of solid product of intercalation of ethanol into $VOPO_4$ at 25 °C. The (001) line of the host is marked H and the (001), (002) and (003) lines of the intercalate are marked I_1, I_2 and I_3

vanadyl phosphate together with an increase of intensity of the (00l) lines of $VOPO_4.2C_2H_5OH$ can be seen in the diffractograms. A time dependence of intensity of the (001) line of the intercalate is given in Fig. 4. It is obvious that this dependence has a distinct sigmoid shape. A more detailed study of intercalation of ethanol into anhydrous vanadyl phosphate will be a subject of further work.

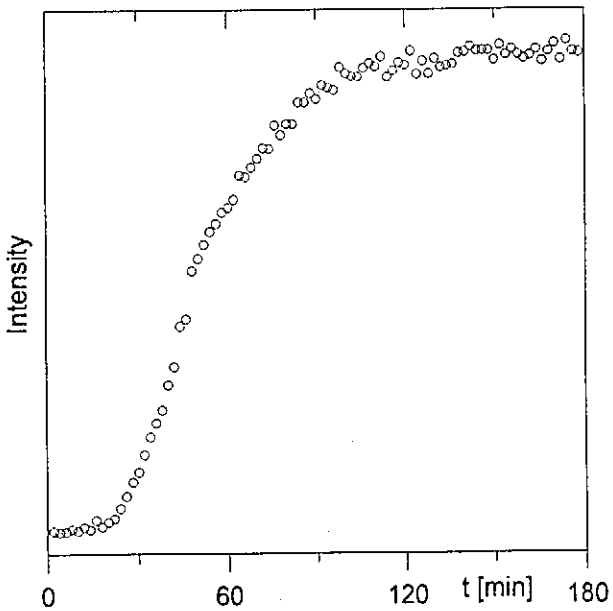

Fig. 4 Time dependence of integral intensity of the (001) line $VOPO_4.2C_2H_5OH$ during intercalation of ethanol into $VOPO_4$

Acknowledgements

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References

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