HIGH-TEMPERATURE MICROPHOTOMETRY AND MICRODILATOMETRY

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Potentionalities are discussed of using the optical microscope combined with a microphotometer and a hot stage for recording automatically the course of temperature changes in minerals and non-homogenous materials, in a temperature range of up to 1,500 °C. The structural and volume changes and reactions are recorded as changes in the intensity of light transmitted through, or partly screened by the preparation. The method of determining temperature-dependent birefringence changes and transmissivity changes is described, as well as the dilatometric method, and examples shown of the use of these methods in various fields of research. Their comprehensive application renders possible a partial quantitative description of phenomena observed visually in the hot stage, extending thus the possibilities of the established thermic methods.

INTRODUCTION

Microscopic examination of a heated material provides ample possibilities of studying decomposition, melting and recrystalization processes, polymorphic transformations, etc. In cement, ceramics and glass research, the examination by transmitted light is of major importance, since, apart from the study of the above processes, it also permits to measure some optical properties [1]. However, the visual examination of processes developing in the heated material mostly provides only less exact information on their kinetics; therefore, new ways how to simultaneously record the value which would better characterize the nature and the course of these processes are being searched for. One of these ways, introduced by R. P. Miller and G. Sommer [1], consists of combinig the hot stage with high temperature D.T.A. The heated thermocouple method [2] which is especially suitable for melts has a drawback due to the rough surface of the specimen; in a medium with a low refractive index this results in a lower quality of the micrograph. The measurement of optical values or the examination by transmitted light of processes taking place in solids at higher temperatures require the preparation of thin sections [3] polished on both sides; if the liquid phase develops later on, examination by light reflected from a platinum plate has to be used [4]. A series of valuable data on the nature and development of processes studied visually when using a microphotometer hot stage may by obtained by recording the change in the intensity of transmitted light. This applies in particular to birefringence changes in crystals, recrystallization of glass, thermic dissociation of substances, development of liquid phase

in polycomponent systems and exact determination of the melting point. Combined with a hot stage and a microphotometer, the optical microscope may also be used as a high-temperature dilatometer.

EQUIPMENT

A Leitz not stage (1350 °C) [5] adapted for a temperature range of up to 1500 °C and attached to a Leitz Ortholux Pol microscope was used. The hot stage is designed as a vertical resistance microfurnace with a Pt-Rh winding and a water jacket. In the inner heated tube of the furnace (Fig. 1) a sintered corrundum tube (*3*) is placed coaxially supporting the lower platinum plate (*4*) with a hole for the thermocouple joint (*5*). The wires of the thermocouple are led from the opposite end of the tube (*3*) past the hole in plate (*4*) so as not to obstruct the observation. Plate (*4*) supports a platinum slide (*6*, *12*), an insert with a larger hole (*8*) or rings (*13*) and an upper platinum plate with a hole (*9*, *15*). The remaining space of the microfurnace is filled with porous Al_2O_3 ring (*10*, *16*) and covered by an upper metal plate (*11*, *17*) cooled through the contact with the water jacket of the stage. Each platinum plate has two small symmetrical openings enabling the plate to be picked up with a forceps. It is thus easy to insert and remove the preparation or to interchange both alternative arrangements. The current for heating the stage is supplied by a

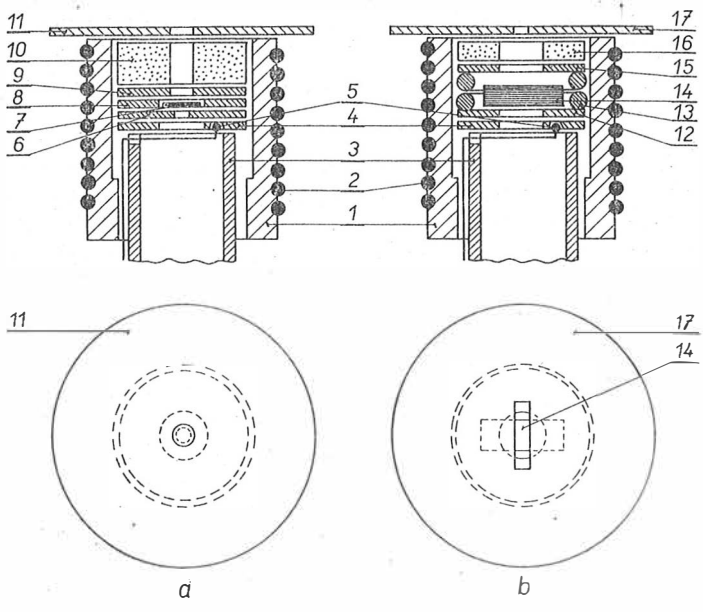

Fig. 1. Arrangement of the hot stage inner space. a — for thin sections and thin preparations, b — for microphotodilatometry; 1 — sintered corrundum tube; 2 — heating coil; 3 — inner sintered corrundum tube; 4 — lower platinum plate; 5 — thermocouple joint; 6, 12, — supporting slide of the preparation; 7 — thin preparation; 8 — platinum insert; 9, 15 — upper platinum plate; 10, 16 — porous Al_2O_3 plate; 11, 17 — upper metal plate; 13 — platinum ring; 14 — test specimen.

variable voltage transformer with a reversible synchronous motor. The transmission to the transformer axis is provided by a closed loop of a steel strand and by a disc with openings permitting the heating and cooling programs to be selected by the location of pins. Due to the small mass of the microfurnace, a satisfactory linearity of the temperature changes in the preparation can be obtained.

For transforming the intensity of light into electric voltage, the photometric part of automatic Quantanal P-20 (6) quantitative analyzer has been used, in combination with the x-y-recorder. This device has the advantage that the diaphragm placed in front of the photomultiplier may be readily exchanged and the size and form of its opening selected. The photomultiplier being removed the image can be seen on the screen.

As the light source a low voltage lamp was used, fed from a controllable stabilized direct supply unit of the Quantanal P-20 apparatus. All measurements were carried out by means of monochromatic light with interference filters inserted between the diaphragm and the photomultiplier; this permitted the preparation to be simultaneously examined in white light. The influence of radiation emitted by the heated preparation had to be suppressed by selecting a suitable wave-length; this is still feasible within the visible part of the spectrum at temperatures ranging to 1200 °C. For temperatures of up to 1500 °C, a wave-length $\lambda = 376$ nm was used for which the intensity of the emitted radiation, compared with that of the transmitted light, in most cases did not reach measurable values. For highly absorbing preparations the background can be established by periodical short time screening of the lighting, and in such cases the records have to be corrected according to the background curve.

With regard to the negligible mass of the preparation, a temperature change of 20 °C/min was used. The microphotometer was fed by a regulated power supply whose stability during the time needed for heating the specimen to 1500 °C or, possibly, for cooling it (150 min.) met all accuracy requirements. The stability of the apparatus was tested by long-term recording of the constant photometric deviation, and its attainment after switching on was always registered graphically. In the course of measurement the stability of the apparatus was checked by comparing the adjusted value of the photometric deviation without the preparation before and after the measurement. Occasional fluctuations, in the course of measurement, which might be due to extraordinary mains voltage variations, are easily discernible in the recording.

All photometric measurements were made with the upper silica glass of the hot stage removed, the transmissivity of silica glass being subject to condensation-dependent changes taking place during the heating. The influence of air convection in the proximity of the preparation was minimized by the internal arrangement of the stage and by the selected size and form of the opening in the upper metal plate of the stage. At higher temperatures, the light refraction in the heated air layer between the hot stage and the objective produced fluctuations in the deviation indicated by the microphotometer. This effect was fully eliminated by placing a small fan at a certain distance from the microscope; condensation on the front lens of the objective was thus simultaneously eliminated and the cooling of the lens improved.

The data furnished by the Pt/10 % Rh-Pt thermocouple were corrected for the real temperature of the preparation according to the β—α quartz inversion and according to the melting points of gold, silver, and diopside.

These temperatures were established by photometry, as will be described further, and a scale of real temperatures for the x—y-recorder was drawn up acording to the correction curve.

TEMPERATURE — DEPENDENT BIREFRINGENCE CHANGES

Preparation of specimens

The thin sections used for measuring birefringence in the hot stage must be well polished on both sides and their thickness selected so that the retardation of the grain sections to be measured do not exceed the value of the wave-length of the light by which the measurement is effected. For this purpose a polished section is fixed on a glass slide with epoxy resin, and the final operation in preparing the section consists then of repeated polishing which (possibly in combination with etching) may reduce the thickness of the thin section to less than 10 μm. The detaching of the thin section is carried out by evaporating the resin at elevated temperature, preferably in a space connected to vacuum pump.

Photometric measurement of birefringence

The relationship between the intensity of light transmited through an optically anisotropic crystal between crossed nicols and the relative retardation of light rays may be used for the photometric determination of birefringence. This method, however, is accurate enough at low retardations only, and only within the first order region it may compete with other accurate methods.

At first, a photometric deviation-retardation curve is constructed by means of a quartz wedge and a compensator. The quartz wedge is placed diagonally in the cross guide on the microscope stage so that its retardation may be compensated e.g. by a Berek compensator. By moving the wedge diagonally, the microphotometer is adjusted for minimum deviation corresponding to retardation $\lambda/2$, and this deviation is adjusted for the whole range of the recorder scale. By moving the wedge, the photometric deviation is adjusted for the first minimum, and moving it gradually back, the deviations of the recorder are recorded and, at the same time, the values of the corresponding retardations measured by the compensator. The compensator remains permanently inserted in the slot of the microscope and, when recording photometric deviations, it is adjusted for zero retardation. The compensation is made according to the minimum deviation of the microphotometer, with the time constant adjusted at a minimum. The measurement is carried out at a wave-length of light used for high temperature recording and the size of the opening in the diaphragm of the photomultiplier is selected with respect to the relationship obtained, which is affected by the optical system of the device employed, as shown in Fig. 2.

When using this diagram in order to determine microphotometry of the amount of retardation, the following procedure is to be adopted:

At zero retardation of the compensator, the grain to be measured is placed in a diagonal position and the resulting retardation is adjusted by the compensator to a $\lambda/2$ value for which the photometric deviation reaches its maximum. The difference between this deviation and that occurring at the extinction

of the microphotometer for the same maximum as when plotting the diagram (Fig. 2). After returning the compensator to the position of zero retardation, the value of retardation A may be read directly from the diagram against the photometric deviation and, the thickness of the thin sections being known, the value of birefringence may be calculated for the wave-length used. (In accurate measurement, this value has to be corrected for the change in photometric deviation due to the inclination of rotating compensators. For this purpose, too, graphical representation of the relationships of the compensator used is recommended).

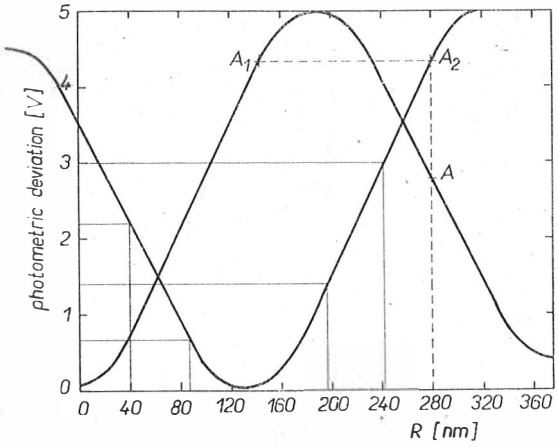

Fig. 2. Photometric deviation [V] retardation relationship (λ = 367 mm) and adjustment of initial retardation by compensator curve; A — initial retardation of the section, A_1 — photometric deviation corrected by compensator, A_2 — starting point of measurement with shifted, curve passing through, R — retardation.

The diagram in Fig. 2 shows that for recording automatically the temperature-dependent changes in birefringence, a temperature range in which the curve in the O—$\lambda/2$ interval is almost linear is the most suitable. Since it is difficult to prepare thin sections with the required retardation value of the crystals to be measured, it is possible by means of the compensator to shift the retardation value into the ●—$\lambda/2$ region, as may be seen in Fig. 2. In such a case, however, when the retardation of the crystal measured decreases to the value for which the correction was made, the photometric deviation reaches its minimum, increasing then with further decrease in retardation. Then the real amount of retardation in the measured grain may be determined by means of the shifted curve, in a manner shown in Fig. 2. The determination of the real retardation in the heated grain by means of a compensator may be substantially simplified by using a transparent. When moving point A to position A_1, by means of the compensator a curve is drawn through point A_2 on the transparent, to which correspond the same amount of retardation and the new photometric deviation. The real retardation corresponding to the photometric deviations recorded during the heating may be found by means of the shifted curve on the original scale of the diagram.

The above technique of converting photometric records into the course of

temperature-dependent birefringence changes requires the measured material to exhibit constant absorption of light, which however, tends to vary at higher temperatures, especially due to surface changes; corrections can be made for temperature-dependent absorption changes recorded at the same wave-length of light.

Arrangement of equipment and measurement

The arrangement of the inner space of the hot stage is shown in Fig. 1a. A thin section fragment is inserted between two platinum plates with hole (*6, 9*), in a space provided by a platinum insert (*8*).

With regard to the size of the grain measured, the size of the circular opening in the diaphragm placed in front of the photomultiplier of the the photometer, as well as the magnification of the lens are chosen so that the surface scanned be representative enough, without risking that its perimeter would get too close to the grain boundary in case of a possible displacement of the thin section. Such a displacement produced by the heat expansion of the micro-furnace, limitates the minimum size of grains whose birefringence can be recorded photometrically as a function of temperature. In the device used for this study, the critical size of grains was about 100 μm. Since in the hot stage the distance between the thin section and the condensor of the microscope is greater, there is an advantage in using a low aperture condensor lens destined originally for a universal stage.

The selection of grain suitable for measurement and the determination of thickness of the thin section in this place by high magnification must be done before the thin section fragment is inserted in the hot stage. In the hot stage, the grain is placed in a diagonal position with the maximum oriented inversely with respect to the compensator, and the photometric deviation of the first maximum, adjusted by the compensator (retardation $\lambda/2$), is modified by the control elements of the microphotometer for the value of the maximum photometric deviation in the diagram of the photometric deviation — retardation relationship. The compensator being moved back to the position of zero retardation, the photometer indicates a deviation corresponding to the actual retardation of the crystal in the thin section. A suitable starting value of photometric deviation is adjusted by the compensator according to the supposed extent of change in retardation under heating, and further temperature-dependent changes in the photometric deviation are automatically recorded after the heating has started.

TEMPERATURE-DEPENDENT CHANGES IN LIGHT TRANSMISSIVITY

When a light beam is transmitted through a continuous medium containing particles of varying refractive indices or consisting only of such particles, its intensity decreases under the effect of diffusion. This decrease in intensity depends on the number of particles and on the relation of their size and distance to the wave-length of the light. When the size of the particles substantially exceeds the wave-lenth of light, diffusion is produced at their boundaries by refraction and reflection. This diffusion increases with the difference in the

refractive indices and with the number of particles. If, for example, air in the intergranular spaces of a pulverous material is replaced by a liquid, the intensity of transmitted light will substantially increase. The refraction and reflection of light at the boundaries of grains involve polarization of light and if the number of particles afflicted by the transmitted light beam is large enough, even optically isotropic non-homogenous material appears the same between crossed nicols as an optically anisotropic material. In such cases also the temperature-deviation curves are similar. The advantage of crossed nicols consists of eliminating the influence of cracks and holes in the preparation, which remain dark, and in the possibility of recording further optical changes.

The measurement of the temperature-dependent changes in light transmissivity may be used for studying the processes of liquation and crystallization of glass, sintering and recrystallization in solid phase, dissociation and dehydroxylation of minerals, formation of partial melt, and reactions in polycomponent systems, etc. However, these curves do not furnish absolute quantitative data. Their interpretation is usually possible only in combination with visual observation. Since this method is highly sensitive to changes in the material tested, it may be regarded as a suitable complement to other thermic methods.

Preparation of specimens and arrangement of equipment

As to the solids of which thin sections can be made, the preparation is the same as when measuring the temperature-dependent changes in birefringence; however, the thickness of the thin section may be greater, owing to light transmissivity. Of fine grained materials, such as e.g. clay minerals, thin and strong plates may be prepared by drying a liquid suspension on an alluminium foil. The detaching of the preparation from the foil may be effected by bending it over an edge. Coarse-grained materials, such as cement and ceramic materials, need to be pressed into thin tablets in steel moulds (Fig. 3). The height of the layer of dry powder *2* on the front of the piston *3* can be adjusted by selecting a suitable insert *5*. When the counter-piston *1* is placed into position, the insert is removed and a thin circular tablet (dia 3 mm) is produced by pressing. The thickness of the tablet is to be selected with regard to the intensity of light used in the microscope and to the composition of material. In this way, even 0.1 mm thick tablets may be obtained.

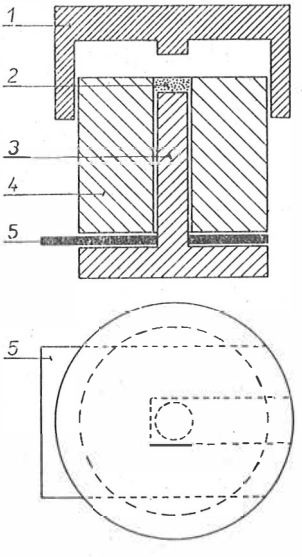

Fig. 3. Mould for pressing thin tablets. 1 — counter-piston, 2 — powder, 3 — piston, 4 — housing, 5 — insert.

For recording temperature-dependent changes in light transmissivity, a large opening in the diaphragm of the photomultiplier and a low-magnification lens were used, in order to obtain the greatest possible light yield and a scanned surface representative with respect to the homogenity of the material. The arrangement of the hot stage is the same as that used for measuring tempera-

ture-dependent birefringence changes (Fig. 1a). When the preparation is melted, the platinum plate must be cleaned in acid or, possibly, ground using abrasive paper.

Measurement

The range of light changes for which the amplification of the signal and the starting point of recording have to be adjusted varies considerably with the nature of the preparation and with the processes developing under heating. As a rule, a first record has to be made under fast heating and slightly increasing the voltage of the photomultiplier; then, according to the result obtained, the positions of the microphotometer and the recorder have to be adjusted. By changing the amplification and by selecting compensatory counter-voltage, it is possible to control the sensitivity in a wide range or, possibly, to specify some interesting parts of the record. In less transmissive preparations or when using lower wave-legnths of light, the value of the photometric deviation due to the emitted radiation is to be determined by periodical short-time screening of the illumination. A background curve is plotted through the points obtained as the design of the microscope allows; visual observation is made simultaneously with the record.

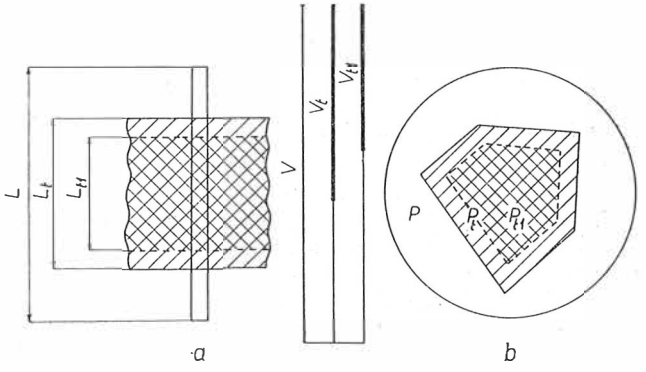

Fig. 4. Diagram of photometric measurement of dilatation; a — linear dilatation, b — area dilatation. Relationships between size and photometric deviations:

$L \sim V$, $P \sim V$,
$L_t \sim V_t$, $P_t \sim V_t$,
$L_{t1} \sim V_{t1}$, $P_{t1} \sim V_{t1}$.

MICRODILATOMETRY

An optical microscope equiped with a microphotometer and a hot stage may easily be modified in order to be used as a high-temperature dilatometer. The volume changes in objects are recorded as changes in the photometric deviation produced by a light beam partly screened by the object. If the beam has two absolutely parallel planes, as when passing through a slot, the photometric deviation will be proportional to the length of its screened part and in this case the dilatation of the object in the direction of the slot (Fig. 4a) will be

$$\Delta L\,[\%] = \frac{L_t - L_{t_1}}{L_t} \cdot 100 = \frac{V_t - V_{t_1}}{V_t} \cdot 100.$$

Similarly, the change in the surface of the object in a plane perpendicular to the axis of the beam (Fig. 4b) will be

$$\Delta P\,[\%] = \frac{P_t - P_{t_1}}{P_t} \cdot 100 = \frac{V_t - V_{t_1}}{V_t} \cdot 100.$$

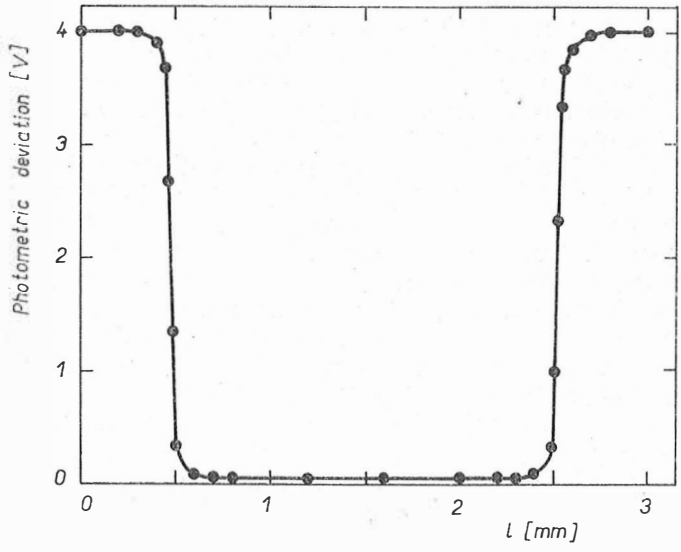

Fig. 5. Light intensity distribution in the plane of the photomultiplier diaphragm, over a line perpendicular to the dilatation of the wire. l — width of object.

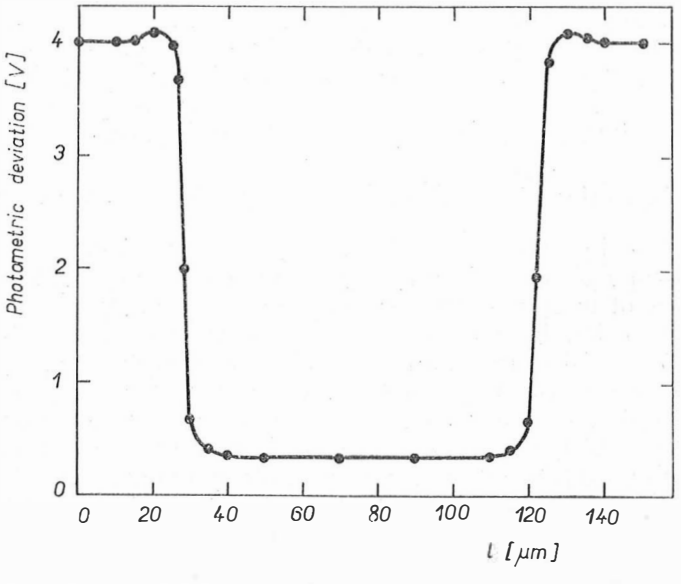

Fig. 6. Light intensity distribution in the plane of the photomultiplier diaphragm, over a line drawn through the center of a pyrite grain. l — width of object.

In reality, however, the object is sufficiently illuminated by the light reflected from the lens and diffraction is taking place at its boundary. .Consequently, the image of the measured object will never be absolutely dark in the plane of the photomultiplier, but will always exhibit a certain degree of illumination, depending on the size of the object and on the wave-length of light.

The distribution of the intensity of illumination over the projection of the object on the diaphragm of the photomultiplier and on its surrounding was measured in practice. As objects there were used wires of various diameter and pyrite grains, placed on a planparallel glass slide on a microscope stage equiped with a micrometric manipulator. Moving the object, the value of the photometric deviation was gradually determined in a line either perpendicular to the dilatation of the object or passing through the center of the isometric grain. The circular opening of the diaphragm of the photomultiplier had a diameter of 0.063 mm; the actual size of the scanned surface is represented in Fig. 5 and 6 by circles around the points of the curves.

As may readily be seen from Fig. 5 and 6, the illumination level of the object is low and practically constant, rising somewhat with its decreasing size. The rounding of the shape of the photometric deviation on the boundaries of the object is due to diffraction and to the final size of the diaphragm opening of the photomultiplier. An increasing illumination intensity was established only at higher magnification when the diameter of the area scanned by the photometer was small enough in relation to the width of the interference bands (Fig. 6). The areas above the curves in Figs. 5 and 6, delimitated from above by the levels of the photometric deviations outside the objects, are proportional to the decrease in photometric deviation occurring after the insertion of objects into the hot stage. Due to the changes in the size of objects, occurring to an extent given by the thermic dilatation, only a parallel displacement of the sheer parts of curves is taking place, the changes in the size of areas reflecting the relative changes in the size of the objects. This means that the change in the photometric deviation, related to its decrease after insertion of the object into the hot stage, will be proportional to the change in the size of the object. The above relationships which were determined geometrically, will hold also in practice for small changes in the size of the object (Fig. 4).

Preparation of specimens and arrangement of equipment

The size of the inner space of the hot stage and the minimum magnification of the microscope permit to use prisms of a size of up to $2 \times 2 \times 6$ mm. Small test specimens of lump material are prepared by grinding. Test specimens of materials with a low light absorption have their upper side formed by two polished surfaces which are at an angle of 90 degrees. The image of these test-pieces in the plane of the diaphragm of the photomultiplier is also dark due to the total reflection of light. Specimens of powdered materials are pressed in a precision ground steel mould. By forcing the piston into the mould at a constant distance, small test specimens of the same shape and volume may be pressed as well as test specimens of the same density in case of the same batch. The small size of specimens allows such compressions to be used that the test pieces pressed of powder materials are strong enough and easy to handle. The test specimens are inserted in the hot stage on a platinum plate with an opening, so that their dilatation is perpendicular to the axis of the slot in the diaphragm of

the microphotometer photomultiplier (Fig. 1b, 4a). In practice, the minimum size of the specimen is limited primarily by its movement in the course of heating, which is due to the dilatation of the heated parts of the hot stage. Because of this, only larger grains may be measured by means of a slot in the diaphragm, i.e. grains whose outline has the two opposite sides straight and approximately parallel. For smaller grains of common shape, the measurement of grain area changes in a plane perpendicular to the optical axis of the microscope seems to be more suitable. The opening of the diaphragm is circular (Fig. 4) and the magnification of the measured grain in the plane of this diaphragm has to be selected so as to allow the projection of the grain — in spite of the latter's dilatation and movement — to remain inside the opening, not approaching too much its periphery.

These small grains are put on a transparent slide whose light transmissivity either does not change within the given temperature range or is determined beforehand. The attainable measurement temperature depends on the beginning of the mutual reaction. Sapphire plates supplied by the hot stage manufacturer are suitable for being used as supporting slides. In preparing the equipment it is necessary to check whether the image observed in the microscope is also sharp at the plane diaphragm. This check is essential especially when using Bertrand lens; it may be carried out by means of a screen placed at the plane of the photomultiplier diaphragm. At the same time, the orientation of the slot has to be examined and its center situated so as to coincide with the center of the cross wire graticule of the eyepiece. The small test specimen is inserted into the hot stage and — under the rotation of the stage — it is put into a position perpendicular to the dilatation of the slot. When using micrometer eyepieces, the specimen is positioned by the centring screws of the hot stage into the center of the field of view so that its image at the plane of the photomultiplier

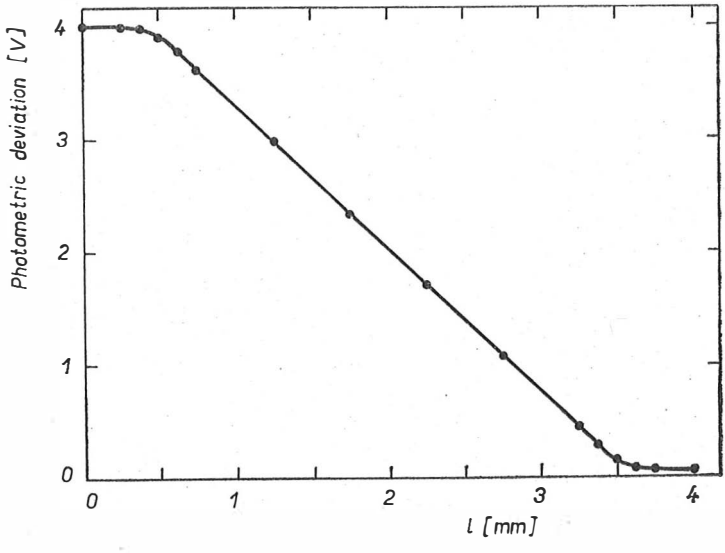

Fig. 7. Light intensity distribution over the length of the slot in the photomultiplier diaphragm. l — length of the slot.

diaphragm covers symmetrically the central part of the slot (Fig. 4a). The relationship between the slot length and the eyepiece scale being known, it is possible for the small test specimens to be correctly placed in the hot stage when the photomultiplier is put on. The slot length and the magnification are chosen with regard to the maximum size of the test specimen during the heating, so as to keep its boundaries within the area of linear dependence of the photometric deviation on the slot length, as will be described in the following.

The relation between the slot and the eyepiece scale remains constant for various magnifications and, hence, the slot length being constant, it is possible to change the lenght of its coverage by the object only by changing the magnification, the photomultiplier being fitted on. This relation, however, being different for the Bertrand lens and for the lens proper, has to be determined individually. The illumination of the field of view in the part which is projected on to the slot must be uniform and special attention must therefore be paid to the centering of the illumination system of the microscope. A very good uniformity as well as an increased intensity of illumination were achieved with the hot stage when using condensors destined for universal stages. The distribution of the intensity of light over the length of the slot in the diaphragm of the photomultiplier was determined by gradually screening the slot by a screen moved micrometrically in the plane of the microscope stage (Fig. 7). An analogical test can be carried out for the circular opening in the diaphragm by screening four times one half of the opening in two directions perpendicular to each other.

Measurement by means of a slot in the photomultiplier diaphragm

The equipment being arranged, the photometric deviation corresponding to the non-screened slot is adjusted for the whole range of the y-axis of the x-y-recorder. This adjustment is carried out with the voltage of the photomultiplier somewhat amplified, in order to enable the amplification reserve to be used for adjusting the sensitivity of the recorder. Upon inserting the measured test specimen into the hot stage and placing it at the center of the field of view, perpendicularly to the dilatation of the slot in the diaphragm of the photomultiplier, the decrease in photometric deviation indicates the initial size of the object to which the measured change will be related.

This value is adjusted by steplessly amplifying the voltage of the recorder of photometer for the whole range of the y-axis of the recorder in such a way that the residual value of the photometric deviation be amplified proportionally.

The sensitivity of the recorder is adjusted by amplifying the voltage of the photomultiplier. Since the residual value of the photometric deviation after amplification would exceed the range of the recorder, it is offset by adequate countervoltage, by the value of which the starting point of the recording is simultaneously fixed with respect to the presumed course of the dilatation curve.

Example: Range of recorder $V = 20$ cm, decrease in photometric deviation after the insertion of the test specimen measured $V_t = 16$ cm; hence, the residual value of the photometric deviation $V_z = 4$ cm. The value of the amplified residual value

$$V'_z = \frac{V}{V_t} \cdot v_z = \frac{20}{16} \cdot 4 = 5 \text{ cm}.$$

For instance, a ten-fold successive amplification will imply that on the vertical axis of the recorder 2 cm will correspond to a 1% change in the size of the test specimen.

Measurement of area changes

In this type of measurement, the temperature dependent change in the projection area of a particle, in the plane of the diaphragm of the photomultiplier, is recorded. In materials with isotropic volume changes the total length change

$$\Delta L\,[\%] = \left(\sqrt[3]{\frac{V + \Delta V}{V}} - 1\right) . 100,$$

the arrangement of the apparatus being similar to that employed in measuring by means of the slot in the diaphragm photomultiplier.

The arrangement employed in measuring area changes may be used for determining the point and the course of melting of microscopic particles. The particles of common shape are changed into a drop of melt, the diameter of which is always different in a plane perpendicular to the optical axis of the microscope. For this purpose, the examination by reflected light and a polished platinum slide may also be used.

EXAMPLES OF APPLICATION OF THE METHODS DESCRIBED

For comparing the results obtained by the methods described, quartz was selected in view of its different polymorphic transformations and the related optical and volume changes. A curve of change in photometric deviation under crossed nicols in a section parallel to the optical axis was constructed with the correction made by a compensator (Fig. 8a) and converted by means of a transparent into a birefringence-temperature relationship (Fig. 8b). The similarity of both curves and the more pronounced shape of the curve in Fig. 8a may readily be seen from the figures. The final value of the photometric deviation is distinctly smaller than the residual value corresponding to the retardation of the compensator, because in the course of the α-quartz — α-cristobalite transformation the absorption of the thin section increases considerably under the effect of cracking. Therefore the cooling curve could not be converted into a birefringence-temperature relationship, and it was not possible to determine the birefringence of β-cristobalite arising in the form of smaller and differently oriented grains. It is evident, however, that the curve of the photometric deviation is characteristic enough for the nature of the three polymorphic transformations. Fig. 8c shows temperature-dependent variations in light transmissivity obtained under parallel and crossed nicols by illuminating thin pressed quartz powder tablets. The shape of both curves is nearly the same up to a temperature of 1250 °C and the β—α-quartz transformation is not recorded. Therefore only changes in the structure of the tablets are recorded within this temperature range; these changes seem to be produced by the volume changes of particles, since in visual examination by white light only changes in the colour of the transmitted light may be observed. The following abrupt rising of the curve obtained without the analyzer seems to be the consequence of the initial sintering whose intensity grows rapidly with

the beginning of the α-quartz — α-cristobalite transformation. A decrease in the intensity of the transmitted light is recorded under crossed nicols as a consequence of the decreasing polarization of light on the quartz particles and of their loss of birefringence. The sintering of the tablet implies substantially increased light transmissivity and therefore even a minor birefringence of β-cristobalite produces a pronounced increase in the photometric deviation during polymorphic transformation.

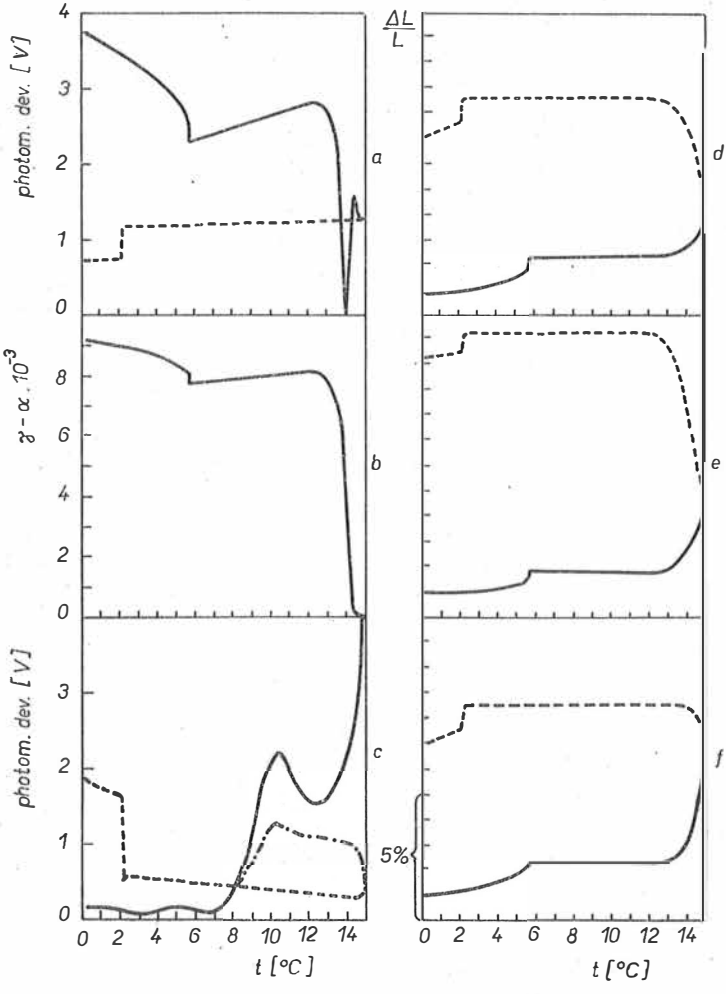

Fig. 8. Micrometric records of temperature changes in quartz (λ = 376 mm, 20°C/min). —— heating, – – – cooling.

a — change in photometric deviation under crossed nicols, section II c (thin section), b — change in birefringence according to curve a, c — change in light transmissivity of a thin tablet pressed of powder, – – – without analyzer, – . – . – with analyzer, d — dilatometric curve in direction c (test specimen ground from a monocrystal), e — dilatometric curve for direction c (test specimen ground from a monocrystal), f — dilatometric curve of a test specimen pressed from powder.

In Fig. 8d, e, dilatation curves are shown of test pieces ground in directions perpendicular to and parallel with the crystallographic c-axis of quartz, and in Fig. 8f a curve in seen of a test specimen pressed from powder of the same crystal. With ground test specimen, the change produced by the α-quartz — α-cristobalite transformation is more pronounced owing to the formation of cracks, in contrast to test pieces made from powder, in which the sintering of particles is conspicuous. In Fig. 9, three examples are shown of decomposition processes during the heating, defined by the change in light transmissivity, as well as a curve obtained for the glass used for manufacturing glass-crystalline material. There is an evident difference between the dissociation of calcite,

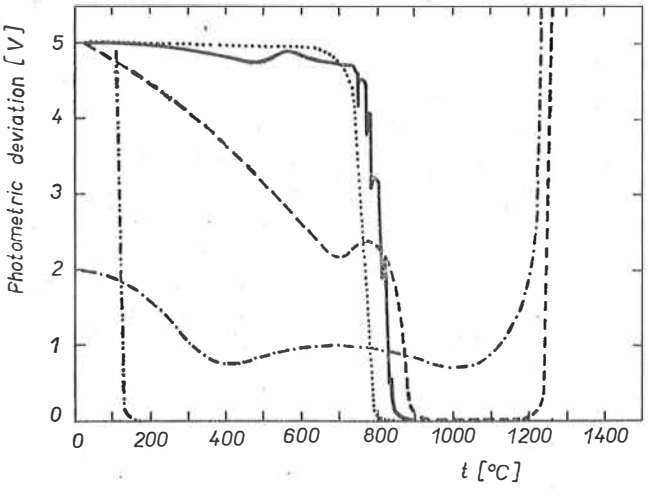

Fig. 9. Temperature-dependent changes in light transmissivity of
–.–.– gypsum, plate according to (010),
. . . . . calcite, plate according to (1011),
——— muscovite, plate according to (001),
– – – – – – – glass, thin section,
–.–.–.– illite Fithian, suspension dried on alluminium foil.

whose course is continuous, and the dehydroxylation of muscovite, characterized by abrupt separation of flakes (001). The light transmissivity curve for glass is reversible up to the first temperature maximum (cca 770 °C) and its decrease in this region seems to be produced by temperature fluctuations and liquation. The following decrease in light transmissivity is irreversible and expresses the course of crystallization, the crystals being visually discernible in the microscope only at temperatures of about 1000 °C. The final rising of the curve is a consequence of the dissolution of crystals and of the melting of the thin section.

The curve for illite shown in Fig. 9 exemplifies a photoelectric record of changes occurring in a ceramic raw material, especially of the formation of a liquid phase during the heating. The test specimen was prepared by sedimentation of a drop of suspended illite on an alluminium foil and the surface of the flakes may therefore be assumed to be oriented perpendicularly to the

optical axis of the microscope. The cause of the decrease in light transmissivity is similar as in the case of muscovite and the shape of the curve exhibits a wide range of dehydroxylation as a consequence of the dispersion of the particle size. The rising of the curve from about 1050 °C corresponds to the formation of the liquid phase, which also takes place in a wide temperature interval, so that it is difficult to determine by other thermic methods.

SUMMARY

The paper deals with the photoelectric recording of temperature-dependent changes occurring in heated microscope preparations and with the application of the optical microscope to microphotodilatometry.

The combination of a hot stage with a microphotometer renders possible to record temperature-dependent changes in the birefringence of crystals and in the light transmissivity of non-homogenous materials in a temperature range of up to 1500 °C. As preparations may be used thin sections ground on both sides, thin tablets pressed from powder material, or thin layers obtained by drying substances suspended in liquids. Under controlled heating the preparation is illuminated by a stabilized source of light and the temperature-dependent change in the intensity of the transmitted light under crossed or parallel nicols is recorded by an x-y-recorder as a change in photometric deviation. By using a compensator, it is possible to choose that region of the photometric deviation which is optimum for measuring the temperature-dependent changes in retardation, and by using a shifted curve plotted on a transparent the conversion into birefringence-temperature relationship may easily be effected.

The recorded temperature dependence of light transmissivity expresses the course of the visually observed processes as well as their instantaneous relative intensity. Examples are listed of the course of the loss of crystalline water in gypsum, the dehydroxylation of muscovite and illite, the dissociation of calcite and the liquation and crystallization of glass.

The dillatation of test pieces and microscopic grains is recorded as a change in the photometric deviation produced by a beam of light of a suitably selected diameter and partly screened by the measured object. The shape and the diameter of the beam is given by the opening in the diaphragm placed in front of the photomultiplier, on which diaphragm the measured object is projected by the optical system of the microscope. The practical delimitation of the influence of diffraction and of light reflection from the frontal lens has proved that in the range of potential dilatations the change in the photometric deviation is proportional to the change in the size of the object. The method described enables dilatometric curves to be constructed for objects larger than 0.1 mm. Examples are listed of dilatation curves for β-quartz in directions perpendicular to and parallel with the c-axis of the crystal, as well as a curve for a test specimen pressed from powder.

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VYSOKOTEPLOTNÍ MIKROFOTOMETRIE A MIKRODILATOMETRIE

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V článku je popsán způsob fotoelektrické registrace průběhu tepelných změn v zahřívaných mikroskopických preparátech a použití optického mikroskopu jako mikrofotodilatometru. Spojení zahřívacího stolku s mikrofotometrem umožňuje registraci změny dvojlomu krystalů a světelné propustnosti i nehomogenních materiálů s teplotou do 1500 °C. Jako preparátů lze použít oboustranně leštěných výbrusů, tenkých tablet, slisovaných z prášků nebo tenkých vrstev, získaných vysušením suspenzí v kapalinách. Preparát je v průběhu řízeného ohřevu osvětlen stabilizovaným světelným zdrojem. Změna intenzity procházejícího světla s teplotou při zkřížených nebo rovnoběžných nikolech je registrována souřadnicovým zapisovačem, a to jako změna fotometrické výchylky. Použití kompenzátoru umožňuje volbu optimální oblasti změny fotometrické výchylky pro měření změny zpoždění s teplotou a použití posuvné křivky na průsvitce usnadňuje převod na závislost dvojlomu na teplotě. Záznam světelné propustnosti na teplotě vyjadřuje průběh procesů, pozorovaných vizuálně, a jejich okamžitou relativní intenzitu. Jsou uvedeny příklady průběhy ztráty krystalové vody sádrovce, dehydroxylace muskovitu a illitu, disociace kalcitu a likvace a krystalizace skla.

Dilatace malých tělísek i mikroskopických zrn je registrována jako změna fotometrické výchylky vyvolané světelným svazkem vhodně voleného průřezu, částečně stíněného měřeným objektem. Tvar a průřez svazku je dán otvorem ve cloně fotonásobiče, na kterou je měřený objekt optickou soustavou mikroskopu promítán. Praktické vymezení vlivu ohybu světla a odrazu od frontální čočky objektivu prokázalo, že v rozmezí možných dilatačních změn je změna fotometrické výchylky úměrná rozměrovým změnám objektů. Popsaná metoda umožňuje pořízení dilatometrických křivek objektů větších než 0,1 mm. Jsou uvedeny příklady dilatačních křivek výchozího β-křemene ve směru rovnoběžném a kolmém ke krystalové ose *c* a křivka tělíska, vylisovaného z prášku.

Obr. 1. Úpravy vnitřního prostoru zahřívacího stolku a — pro výbrusy a tenké preparáty, b — pro mikrofotodilatometrii; 1 — trubka ze slinutého korundu, 2 — topné vinutí, 3 — vnitřní slinutá korundová trubka, 4 — spodní platinová destička, 5 — svar termočlánku, 6, 12 podložka preparátu, 7 — tenký preparát, 8 — platinová vložka, 9, 15 — svrchní platinová destička, 10, 16 — vložka z porézního Al_2O_3, 11, 17 — svrchní kovová deska, 13 — platinový kroužek, 14 — tělísko.

Obr. 2. Závislost fotometrické výchylky [V] na zpoždění ($\lambda = 367$ nm) a nastavení výchozího zpoždění kompenzátorem pomocí posunuté křivky; A — původní zpoždění řezu, A_1 — fotometrická výchylka, opravená kompenzátorem, A_2 — výchozí bod měření s proloženou posunutou křivkou, R — retardace.

Obr. 3. Forma na lisování tenkých tabletek; 1 — protipíst; 2 — prášek, 3 — píst, 4 — pouzdro, 5 — vložka.

Obr. 4. Schéma fotometrického měření dilatace; a — lineární, b — plošné. Vztahy mezi rozměry a fotometrickými výchylkami:

$$L \sim V, \qquad P \sim V,$$
$$L_t \sim V_t, \qquad P_t \sim V_t,$$
$$L_{t1} \sim V_{t1}, \qquad P_{t1} \sim V_{t1}.$$

Obr. 5. Rozložení světelné intenzity v rovině clony fotonásobiče v linii, kolmé k protažení drátu; l — šíře objektu.

Obr. 6. Rozložení světelné intenzity v rovině clony fotonásobiče v linii, procházející středem pyritového zrna; l — šíře objektu.

Obr. 7. Rozložení světelné intenzity po délce štěrbiny ve cloně fotonásobiče; l = délka štěrbiny.

Obr. 8. Mikrofotometrické záznamy tepelných změn křemene (λ — 376 nm, 20 °C/min). — ohřev, - - - chlazení, a — změna fotometrické výchylky při zkřížených nikolech, řez rovnoběžný s osou c (výbrus); b — změna dvojlomu podle křivky a, c — změna světelné propustnosti tenké tabletky, vylisované z prášku, — bez analyzátoru; —.—.—. s analyzátorem, d — dilatometrická křivka směru c (tělísko, vybroušené z monokrystalu), e — dilatometrická

křivka směru c (tělísko, vybroušené z monokrystalu), f — dilatometrická křivka tělíska, vylisovaného z prášku.

Obr. 9. Změna světelné propustnosti s teplotou;
–..–..– sádrovec, destička podle (010),
. . . . . kalcit, destička podle (1011),
———— muskovit, destička podle (001),
– – – – – – sklo, výbrus,
–.–.–. illit Fithian, suspenze, vysušená na hliníkové fólii.

ВЫСОКОТЕМПЕРАТУРНАЯ МИКРОФОТОМЕТРИЯ И МИКРОДИЛАТОМЕТРИЯ

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В статье описывается способ фотоэлектрической регистрации хода изменений температуры в нагреваемых микроскопических препаратах и использование оптического микроскопа в качестве микрофотодилатометра. Соединение нагревательного столика с микрофотометром дает возможность регистрировать изменения двойного лучепреломления кристаллов и светопроницаемости также и у неоднородных материалов при температуре до 1500 °C. В качестве препаратов можно применять лощенные с обоих сторон шлифы, тонкие таблетки, спрессованные из порошков или тонких слоев, полученных высушиванием взвеси в жидкостях. Препарат в ходе управляемого обогрева освещается стабилизированным источником света, и изменение интенсивности проходящего света по мере изменения температуры при перекрестных или параллельных николях записывается координатным самописцем как изменение фотометрического отклонения. Применение компенсатора дает возможность избрать оптимальную область изменения фотометрического отклонения для измерения изменения задержки согласно температуре, а применение смещенной кривой на кальке облегчает перевод на зависимость двойного лучепреломления от температуры. Зависимость светопроницаемости от температуры выражает ход визуально наблюдаемых процессов и их мгновенную относительную интенсивность Приведены примеры процессов потери кристаллической воды в гипсах, дегидроксилации мусковита и иллита, диссоциации кальцита и ликвации и кристаллизации стекла.

Дилатация малых телец и микроскопических зерен регистрируеся как изменение фотометрического отклонения, вызванного пучком лучей выгодно избранного сечения, частично экранированным измеряемым объектом. Форма и сечение пучка даны отверстием в диафрагме фотоумножителы, па которую измеряемый объект проектируется оптической системой микроскопа. Практическое определение влияния дифракции света и отражения от фронтальной линзи объектива доказало, что в пределах возможных дилатационных изменений изменение фотометрического отклонения будет пропорциональным изменениям размеров исследуемых объектов. Описанный метод дает возможность создать дилатометрические кривые объектов, превышающих 0,1 мм. Приведены примеры дилатационных кривых исходного бета-кварца в направлениях параллельном и перпендикулярном к оси кристалла *c* и кривая головки, спрессованной из порошка.

Рис. 1. Приспособление внутреннего пространства нагревательного столика. a — для шлифов и тонких препаратов, b — для микрофотодилатометрии: *1* — трубка из спекшегося корунда, *2* — накальная обмотка, *3* — внутренняя трубка из спекшегося корунда; *4* — нижняя платиновая трубка, *5* — сварной шов термоэлемента, *6, 12* подкладка препарата, *7* тонкий препарат, *8* — платиновый вкладыш, *9, 15* — верхняя платиновая плитка, *10, 16* — вкладыш из пористой окиси алюминия, *11, 17* — верхняя металличестая плита, *13* — платиновое кольцо, *14* — головка.

Рис. 2. Зависимость фотометрического отклонения (V) от задержки ($\lambda = 367$ nm) и установки исходной задержки компенсатором при помощи смещенной кривой; A — начальная задержка сечения, A_1 — фотометрическое отклонение, исправленное компенсатором, A_2 — исходная точка измерения со смещенной кривой, R — задержка.

Рис. 3. Форма для прессования тонких таблеток; *1* — контрпоршень, *2* — порошок, *3* — поршень, *4* — втулка, *5* — вкладыш.

Рис. 4. Схема фотометрического измерения дилатации; a — линейная, b — плоскостная. Соотношения между размерами и фотометрическими отклонениями:

$$L - V, \qquad P - V,$$
$$L_t - V_t, \qquad P_t - V_t,$$
$$L_{t1} - V_{t1}, \qquad P_{t1} - V_{t1}.$$

Рис. 5. Расположение интенсивности света в плоскости диафрагмы фотоумножителя в линии, перпендикулярной к проволоке; l — ширина объекта.

Рис. 6. Расположение интенсивности света в плоскости диафрагмы в линии, проходящей через центр зерна пирита; l — ширина объекта.

Рис. 7. Расположение интенсивности света подлине щели в диафрагме фотоумножителя; l — длина щели.

Рис. 8. Микрофотометрические записи термических изменений кварца (λ = 376 nm, 20 °C/мин.), —— обогрев, — — — охлаждение. *a* — изменение фотометрического отклонения при перекрестных николях, сечение, параллельное с осью *c* (шлиф), *b* — изменение двойного преломления по кривой *a*, *c* — изменение светопроницаемости тонкой таблетки, спрессованной из порошка, —— без анализатора, –.–.–.– с анализатором; *d* — дилатометрическая кривая направления *c* (головка, отшлифованная из монокристалла) *e* — дилатометрическая кривая направления *c* (Головка, отшлифованная из монокристалла), *f* — дилатометрическая кривая головки, спрессованной из порошка.

Рис. 9. Изменение светопроницаемости с температурой;

–..–..– гипс, пластинка по (010),
. . . . . кальцит, пластинка по (10$\bar{1}$1),
———— мусковит, пластинка по (001),
– – – – стекло, шлиф,
–.–.–.– иллит Fithian, взвесь, высушенная на алюминиевой фольге.