STANISŁAW KAŁUŻA[1], ZBIGNIEW SZCZEŚNIAK[2]

Kielce University of Technology
25-314 Kielce, Poland
[1]The Chair of Physics, e-mail: fizsk@tu.kielce.pl
[2]Department of Automatics Devices and Systems, e-mail: Z.Szczesniak@tu.kielce.pl

STABILIZED TEMPERATURE MEASUREMENTS BASED ON THERMOOPTIC MEMORY PHENOMENA

Investigations of non-linear phenomena in A_2MX_4 (where: A - organic cation or ion of alkaline metal, M - metal, X - halogen) crystals with incommensurate phases are very interesting both from scientific and practical point of view. Some aspects of applications of these crystals to different fields of science and technology are discussed. Thermal hysteresis of birefringence and absorption coefficient, piezooptic, thermooptic and electrooptic effect are observed in selected A_2 MX_4 crystals. This suggests that these materials could be used in temperature measurements by optical methods.

Keywords: optoelectronics, A_2MX_4 type crystals, incommensurate phases, non-linear phenomena, temperature sensors

1. INTRODUCTION

Over the recent years, a quick development in information processing optical methods and measurement methods has been observed. It is therefore extremely important to look for new materials that possess useful optical properties. Contactless optical methods of temperature and electric field measurement are based on the use of semiconductors and optically transparent dielectrics. The latter are represented by, e.g. ferroelectric crystals of A_2MX_4 type with incommensurate phases [1 - 4]. In the above formula, A is an ion of alkaline metal or an organic cation, M - metal (e.g. Zn, Cu, Co, Mn, Fe, Cd, Be), X - halogen (Cl, Br, F, J). The crystals are grown from water solutions [5]. Samples of 1cm×1cm×0.5cm are fairly easy to obtain. Depending on the metal ion, crystals differ in colour: e.g. crystals containing zinc are colourless, those with copper are green, with manganese - light pink and with iron - amber. Structure modulations, including incommensurate modulations are observed in these crystals [1, 3, 6]. The basic disadvantage they have is hygroscopicity.

2. POSSIBLE APPLICATIONS OF A_2MX_4 CRYSTALS OPTICAL PROPERTIES

Temperature sensors are presented below that make use of non-linear optical phenomena characteristic of A_2MX_4 crystals with incommensurate phases.

2.1. Measurement methods

The basic methods in research on A_2MX_4 crystals are optical methods of measurements of absorption coefficient, absorption spectrum and birefringence as temperature function [1]. The spectrophotometric measurement of absorption spectra is carried out with the measurement set which consists of a light source (helium or xenon lamp and the like), an optical spectrometer with spectrum recording system and a cryostat which ensures the sample will have appropriate temperature. Birefringence measurement by the Senarmont method makes use of the change in light polarisation at birefringence centre. The measurement apparatus includes a light source and a detector, polarizer and analyser and a sample located in the optical cryostat.

2.2. Thermooptic effect

The phenomenon of temperature affecting optical properties is called a thermooptic effect. It could be useful while designing various temperature measurement devices. Examples of thermooptic effect measurements have been already presented in the literature on the subject [1, 7, 8].

2.3. Thermal hysteresis

A very interesting effect which results from modulated structures and numerous phase transitions present in A_2MX_4 crystals is the absorption coefficient hysteresis and birefringence hysteresis, which occur in certain temperature ranges. The result is that when a heated sample regains the temperature it had originally, it demonstrates optical properties different from those it used to have. Thermal hysteresis and its width on the temperature scale depend on the existence of modulated structures, in particular on the incommensurate phase occurrence. The phenomenon is observed in many crystals of A_2MX_4 type. In a K_2ZnCl_4 crystal (without Co impurities), the incommensurate phase exists in the 403 - 553K range and hysteresis occurrence covers the phase zone to a large extent. Birefringence thermal hysteresis causes the so-called thermooptic memory phenomenon. The crystal heated from the initial temperature T_p to the temperature T_k and then cooled to the temperature T_π changes the birefringence value by $\delta(\Delta n)$, but this value could be different for various T_k. In the case of the crystal $K_2Zn_{0,9998}Co_{0,0002}Cl_4$, the difference in birefringence coefficient values for heating and cooling is of the order of 10^{-5}, at the same time, for annealed samples the difference is almost constant in a wide range of temperatures [1].

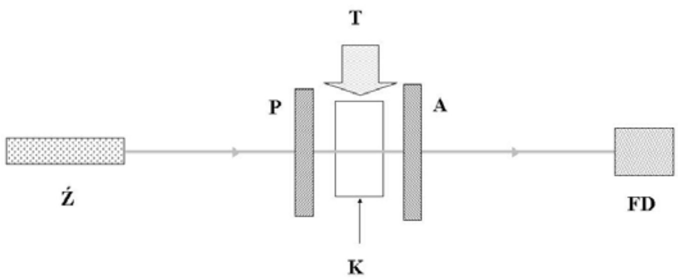
3. TEMPERATURE SENSOR BASED ON THERMOOPTIC EFFECT

Temperature measurement involves recording changes in the intensity of a light beam propagating through a crystal located at the temperature measurement point [7]. As the crystal does not change the refractive index, yet it does change the birefringence value, it must be placed between the polarizer and the analyser. The laser light is polarised by the polarizer (at the angle 45° to the crystallographic axis).

In the birefringent crystal, an ordinary ray and an extraordinary ray of approximately the same amplitudes propagate at different velocities. The difference in optical paths is expressed by the dependence (1):

$$\Delta\gamma = \frac{2\pi}{\lambda}\Delta n d\,, \tag{1}$$

where: λ - wavelength, Δn - crystal birefringence at room temperature, d - sample thickness.



Ź - light source; **P** - polarizer; **A** - analyser; **T** - temperature; **K** - A_2MX_4 crystal; **FD** - photodetector

Fig.1. Diagram of the optical system for temperature measurement.

The change in temperature is accompanied by the value Δn increased by $\delta(\Delta n)$, which affects a change in optical paths by $\delta(\Delta\gamma)$, which in turn changes the initial beam polarisation. The beam having passed through the crystal enters the other polarizer, where it is partially attenuated to a degree that depends on polarization plane rotation. Then the beam incident on the photodetector is transformed into a proportional electric signal.

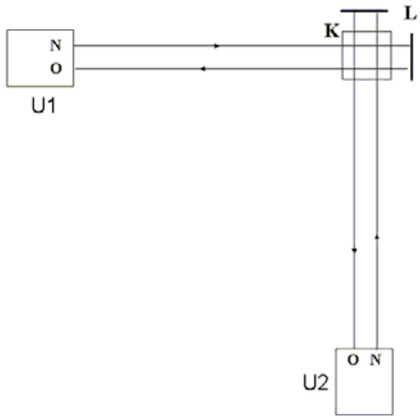
If the angle between the polarizer and the analyser equals $\Delta\gamma/2$ and when Fresnel reflection is disregarded [8], the power output of the light beam is expressed by the dependence (2)

$$I_{wy} = I_{we} \cos^2\left(\frac{\delta(\Delta\gamma)}{2}\right). \tag{2}$$

On the basis of the dependence (1) and (2) it can be concluded that the power recorded by the detector depends on birefringence changes caused by temperature. For instance, for the crystal Cs_2CdBr_4, the birefringence increment amounts to approx. 4 10^{-5}/K for the wavelength λ = 632nm [9]. If the sample thickness is assumed to be 0.2 cm, we obtain $\delta(\Delta\gamma) \approx 45^{\circ}$. The power output decreases by half at a temperature increase by 1K and it virtually disappears at a temperature increase by 2K. Further temperature changes cause cyclic changes in the light power. The example shows that the system can be used for precise temperature measurement within a very small range. It can also constitute a part of a larger system for temperature stabilisation. While designing a device, the crystal thickness (as it affects the measurement range) as well as birefringence characteristics as a temperature function (non-linear dependence zones) must both be taken into account. In order to avoid the error resulting from changes in the air transparency, two beams might be transmitted, one of which could be passing near by the crystal (the reference beam). The temperature would be determined from the ratio of intensity of both beams.

Another possible solution is a reflection mirror placed at the sample. The advantage offered by this option results from the fact that the light goes through the sample twice, so the sample can be twice thinner (whereas the measurement accuracy increases twice). In such a system it is necessary to align the laser beam so that after reflection it would pass to the photodetector.

A_2MX_4 crystal anisotropy provides another promising approach. For the crystal Cs_2CdBr_4 in the incommensurate phase, the temperature change can be accompanied by a birefringence increase (axis c) or decrease (axes a and b) [9]. If two light beams go through an appropriately positioned crystal, the power of one beam can decrease and that of the other one increase when the temperature changes. The differential signal from two photodetectors can become the measurement signal. With such a solution, it is possible to obtain even higher measurement accuracy.



U1, U2 - sending-receiving systems; **N** - transmitter (light source);
O - receiver (photodetector); **K** - A_2MX_4 crystal; **L** - mirror

Fig. 2. Crystal anisotropy application to measurement sensitivity enhancement.

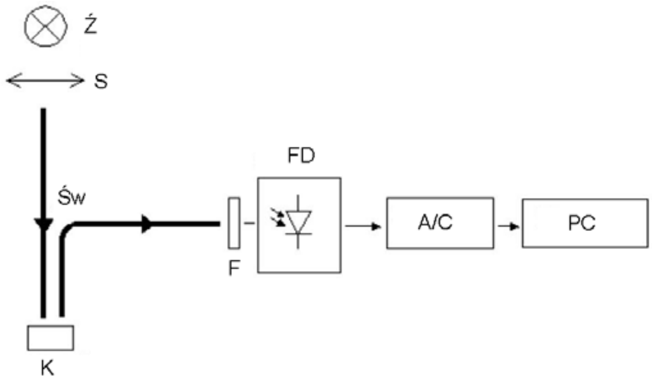
4. TEMPERATURE HYSTERESIS PHENOMENON

In some cases, the phenomenon of temperature hysteresis of changes in the difference between the refraction coefficients of the ordinary ray and extraordinary ray can be applied to temperature detectors. It is assumed that a hypothetical crystal has got a clear and almost ideal temperature hysteresis in the range T_p - T_k and also that the hysteresis is known for a given sample. The initial ambient temperature should range from T_p to T_k. The crystal sample placed at a hardly accessible measurement point becomes the sensor. The concept underlying the measurement is that we should measure the optical properties of the sample that was previously heated at the measurement point. If those properties differ, it means that the temperature has exceeded the boundary value T_k, which can be employed to give warnings or to control the critical value of temperature. The advantage the method has is that the measurement is totally contactless, but it also has a drawback, namely the measurement is not conducted in an interactive fashion.

5. THERMOCHROMIC EFFECT

The thermochromic effect involves a change in the position of individual atoms in the crystalline lattice under the influence of temperature, which is connected with phase transition [10]. The changed crystal structure caused a change in the incident light reflection coefficient which leads to a change in the crystal hue. The phenomenon is observed in many substances, among others in salts Cu_2HgI_4, Ag_2HgI_4 [11], aqueous-alcoholic solution of cobalt chloride [12] as well as some cholesterolic liquid crystals.

The thermochromic effect is observed for the crystal $[NH_2(C_2H_5)_2]_2CuCl_4$ [10, 13]. Green is the crystal natural hue but the sample turns yellow while heated in the temperature range 46^o - 48^oC. When cooled, the crystal returns to the original hue much longer, as it is only at approx. 40^oC that the whole of it recovers the green colour. Thermochromic effect in crystals $[NH_2(C_2H_5)_2]_2CuCl_4$ can be used in temperature detectors of a set value. The crystal hue change results in a change in the spectrum distribution of the reflected light. The latter is recorded by a photo-sensitive detecting element and transformed into an electric output signal. The light from the source of the definite spectral distribution is conveyed to the optical fibre through the lens. The beam is reflected from thermochromic material, for example the crystal $[NH_2(C_2H_5)_2]_2CuCl_4$. The reflected light spectrum depends on the temperature at which the sample is. Owing to the filter, the wavelengths conveyed to the photodetector are those for which the reflection coefficient difference is the highest. After analogue-to-digital conversion, the electric signal becomes the measure of temperature value. Due to the type of the thermochromic effect in the crystal $[NH_2(C_2H_5)_2]_2CuCl_4$, it is possible to build a two-state sensor which reacts to the temperature exceeding 46 - 48°C.



Ź - light source; **S** - lens; **Św.** - optical fibres; **K** - A_2MX_4 crystal; **F** - optical filter; **FD** - photodetector; **A/C** -analogue-to-digital converter; **PC** - computer

Fig. 3. Principle of operation of thermochromic effect based sensor.

6. STABILISED TEMPERATURE MEASUREMENT METHOD BASED ON THERMOOPTIC MEMORY EFFECT

The temperature measurement method presented in this section contains some components, the novelty of which is related to the use of optical techniques for measurements. The method could be applied in order to determine a stabilised temperature at the sites to which access is impossible as regards optics or mechanics. The optical methods of temperature measurement that have been available so far rely on the thermosensitive element in the form of a birefringent crystalline plate through which plane polarised light is shone and the temperature is stated on the basis of changes in the light parameters.

These methods are quite onerous, another drawback is that the measurement accuracy is low, which is connected with the fact that the sensor is placed inconveniently with respect to the measured object. Furthermore, the measurements of optical characteristics are carried out with the systems relying on a physical or mechanical connection with the object where the temperature is measured, which sometimes is not possible.

The invention aims at providing a possibility of taking temperature measurements under unfavourable optical and mechanical conditions. In the method put forward, a crystal with incommensurate phase, which demonstrates the thermooptic memory effect is used as the temperature sensor. It is made in the form of plates (5 x 5 x 1 mm) cut out of the crystal, perpendicularly to one of the main crystallographic directions.

Sensors are put down at the measurement site, where they remain for a given time. They are then removed and placed at the optical set whose task is to measure the birefringence temperature dependence. The dependence $\Delta n_i = f(T)$ is characterised by anomalies specifying the termooptic memory of the crystal. Temperature position of anomalies corresponds to the unknown stabilised temperature of the measured object. The time necessary for the annealing of a given crystal is determined experimentally. For instance, in the case of K_2ZnCl_4, it is approximately 25-30 min. A birefringence measurement must necessarily be conducted in the mode (of cooling or heating) in which the temperature sensor reached the unknown stabilised temperature. Otherwise temperature hysteresis should be taken into account, which lowers the measurement accuracy. With sensors made of K_2ZnCl_4 crystals it is possible to take temperatures ranging 400 - 550 K. By selecting various incommensurate crystals an arbitrarily wide temperature range can be covered. The method ensures a temperature measurement accuracy of approx 0.25 K.

6.1. Temperature sensor

The crystal-optic temperature signalling device is designed to operate in temperature signalling systems at sites to which access is difficult [1, 14].

The temperature signalling device (Fig. 4.) consists of the successive components arranged in the path of the light ray: monochromatic light source 1, condenser 2, linear polarizer 3, thermosensitive element 4, linear analyser 5, crossed with polarizer 3, photon absorbing system with indicator 6. The thermosensitive element is composed of two identical birefringent plates A and B crossing each other. They are cut out from one crystal with incommensurate phase and positioned diagonally. For the arrangement of the optical elements presented above, the photon recording system records the minimum signal at the output of the optical system due to the temperature compensation of plates birefringence.

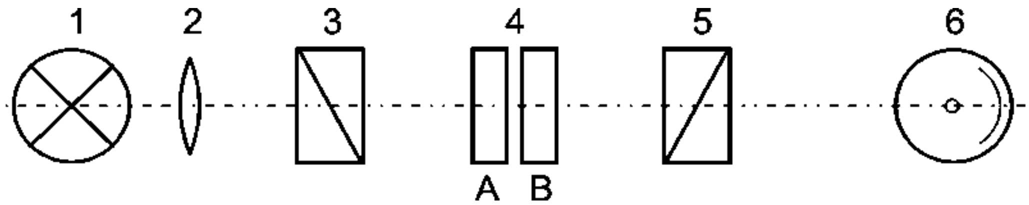


Fig. 4. Structural diagram of temperature signalling device.

If one of the plates, for instance plate A, is annealed in the incommensurate phase at the temperature that has been stabilised for some time sufficient for the thermooptic memory effect to appear and later the plate is placed as in the diagram (Fig. 4), when the temperature changes while the thermosensitive element 4 goes through the stabilisation temperature, in the crystal plate A birefringence the anomaly appears due to thermooptic memory effect. The photon recording system records a sharp increase in the signal. For the sake of optical control, it is also necessary for the difference in optical paths to increase at least $\lambda/2$. For $\lambda = 633$ nm, $\delta(\Delta n) = 10^{-5}$ this condition corresponds to the crystal plate thickness $d_k = 3$ cm. With such plates it is very difficult to prevent temperature gradients deteriorating the signalling accuracy. In order to obtain the difference in optical paths $0.1\cdot\lambda/2$, necessary for clear recording with a photon recording system under such initial conditions, the sufficient plate thickness is of the order of 3 mm, which is easily available in practice. The effective plate thickness can be increased owing to the deposition of reflecting layers and the ray multiple passage through the crystal. Distances between optical elements are not fixed but we can choose them to meet the needs. At sites which are not easily accessible, the light ray can be conveyed to and from the thermosensitive element by optical fibre. In order to guarantee high accuracy of temperature signalling and to avoid temperature hysteresis, the temperature signalling device should be operating in the same mode (of heating or cooling) in which the temperature stabilisation proceeds.

Re-setting the temperature signalling device so that it could signal a different temperature is achieved by means of annealing either of the two crystal plates at appropriate temperatures for as long as necessary for the thermooptic memory effect to appear. Another option available here is to either apply an electric field or subject the plate to uniaxial mechanical stress.

7. CONCLUSIONS

The paper presents the prospects of applying new crystals of A_2MX_4 type that are optically active and have incommensurate phases, to various methods of temperature measurement. The concepts the temperature sensors are based on require further investigations into other crystals of A_2MX_4 type. Special attention should be paid to temperature impact on very small changes in birefringence. This issue is vital for accurate temperature measurement and also for taking into account thermal compensation while measuring the electric field.

REFERENCES

1. Połowinko I., Kałuża S.: *Optical Properties of Incommensurate Phases of A_2MX_4 Type Crystals*. Kielce University of Technology Publishing House, 1998, PL ISSN 0239 – 4979. (in Polish)
2. Kałuża S., Suchańska M., Połowinko I.: *Studies of Absorption Spectra of A_2BCl_4 (B=Cu,Co) Crystals with Organic Cations.* Ferroelectrics, 2000, vol. 239, pp.189-196.
3. Kałuża S., Suchańska M., Belka R., Leśniewski S.: *The Phase Transitions in Ferroelectric Crystals of A_2BX_4 and AMX_3 type*. Ferroelectrics, 2002, vol. 273, pp.143-148.
4. Suchańska M., Kałuża S., Leśniewski S.: *Some Aspects of Using the A_2BX_4 Crystals with Incommensurate Phases in Digital Recording.* Optoelectronic Review, 2001, vol. 9, pp.353-355.
5. Suchańska M., Kałuża S., Belka R., Płaza M.: *Possibilities and Limitations of A_2MX_4 and AMX_3 Crystals Growth.* Proceedings of SPIE, 2003, vol. 5036, no.7, pp.242-247.
6. Suchańska M., Kałuża S.: *Properties of Crystals with Incommensurate Phases*. Elektronika, 2002, no.10, pp. 5-8. (in Polish)
7. Belka R.: *Prospects of A_2MX_4 Crystals Applications to Temperature Measurements*. III all-Poland Doctoral Course Workshop OWD 2001 Istebna - Zaolzie, PTETiS Conference Archives, vol.12, 2001, pp. 213-218. (in Polish)
8. Helsztyński J. et al.: *Laboratory of Rudiments of Optoelectronics and Optoelectronic Metrology*. OWPW, Warszawa, 1997. (in Polish)
9. Vlokh O.G., Kamińskij B.W., I. Połowinko I., Sweleba S.A.: *Opticieskije issledowania niesorazmiernoj fazy w kristałłach Cs_2CdBr_4.* UFZ, 1988, vol.33, no.5, pp.708 - 713. (in Russian)
10. Połowinko I., Kałuża S., Korczak Yu., V. Kapustianik V.: *Thermochromic Properties of A_2CuCl_4 Crystals,* Molecular Physics Reports, 1997, vol. 18/19, p.67.
11. Hughes J.G.: *Thermochromic Solids*. J. Chem. Educ., 1998, vol.75, p.57.
12. Michalski L., Eckersdorf E., Kucharski J.: *Termometrology - Devices and Methods*. Łódz University of Technology Publishing House, Łódź 1998. (in Polish)
13. Belka R., Suchańska M., Kałuża S.: *Prospects of $[NH_2(C_2H_5)_2]_2CuCl_4$ Crystal Applications to Temperature Sensors* (in Polish). VII Scientific Conference: Optoelectronic and Electronic Sensors, Rzeszów 2002, Conference Proceedings, vol. II, pp. 67-70.
14. Gniadek K.: *Information Optical Processing*. PWN, Warszawa, 1992. (in Polish)

POMIARY STABILIZOWANEJ TEMPERATURY W OPARCIU O ZJAWISKO PAMIĘCI TERMOOPTYCZNEJ

Streszczenie

Badania zjawisk nieliniowych w kryształach typu A_2MX_4 (gdzie: A - kation organiczny lub jon metalu alkalicznego, M - metal, X - chlorowiec) z fazami niewspółmiernymi są bardzo interesujące zarówno z poznawczego jak i praktycznego punktu widzenia. W pracy zostały przedyskutowane pewne aspekty zastosowań tych kryształów w różnych dziedzinach nauki i technologii. W wybranych kryształach typu A_2MX_4 są obserwowane takie zjawiska jak: termiczna histereza dwójłomności i współczynnika absorpcji, zjawiska piezooptyczne, termooptyczne i elektrooptyczne. Sugeruje to zastosowanie tych materiałów w pomiarach temperatury metodami optycznymi.