Photochromic effects in sillenite single crystals

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ABSTRACT

Purpose: The aim of this work was to fabricate the doped with transition or rare earth metals the single crystals such as $Bi_{12}GeO_{20}$ (BGO) and $Bi_{12}SiO_{20}$ (BSO), showing the photochromic effect and to study this effect.

Findings: To the study results we can count the development of the mentioned single crystal technology and the measurement set as well as the interpretation of the obtained absorption spectra.

Research limitations/implications: Among others we have found that the photochromic effect in these materials is connected with the change in doped atom charge state by one electron ie. $Mn^{+4} \rightarrow Mn^{+5}$ and $Cr^{+3} \rightarrow Cr^{+4}$. We also propose the schematic presentation of the energetic levels obtained on the basis of the above remarks.

Originality/value: The authors show, for the first time, the photochromic effect in doped with transition or rare earth metals the BGO and BSO single crystals and developed the model explaining this effect. The similar studies were performed on the BTMO (T=Ti, M=Pb) mixed crystals. The applications are connected with the areas of scientific studies of some single crystals as well as using them in particular devices.

Keywords: Single crystals; Sillenites; Photochromic effect; Optical absorption

PROPERTIES

1. Introduction

The photochromic effect is a reversible process of absorption changes in some materials. The changes can be removed and the absorption can be brought into its initial value by means of illumination as well as by annealing. J. Fritzche was the first who described in 1867 the effect which at that time was called the phototropic effect. The description concerned the orange tetracen solution and its decolouration under influence of solar illumination and this colour reappeared in the dark. Then in 1876 E. ter Meer indicated that the colour of dinitro metan salts changes when illuminated. It can be also mentioned the information in the Chemical News (1881) about mystery dye which during day was black and at night white. A manufacturer of the dye defined it as „a dye on the basis of zinc". As a result we can state that the studies on the photochromic effect were initiated at the fall of 19th century. At present we know a large number of inorganic and organic compounds indicating this effect [1], and attention to their investigation has been growing especially during the last 50 years.

As usually, the studies evaluated from qualitative to the quantitative form, the beginning of which can be found in the papers published in twenties of the 20th century. The special attention was devoted to the colour centres in ionic crystals which can be assessed as a basic research leading to the better understanding of many physical processes occurring in the solid state materials, especially the role the point defects play in these materials. During the next decades (1930-1950) the photochromic effect was observed in rutyl (TiO_2) and titanates of alkallic metals and later on (1970-1980) much attention was taken to calcium fluoride doped with elements of rare earth and calcium titanate

single crystals and stroncian (CaTiO$_3$ and SrTiO$_3$) doped with transient metals. At the fall of the 20th century the applications of the photochromic effect have been found.

In our laboratory we for the first time in 1979 discovered the photochromic effect in the appropriate doped Bi$_{12}$GeO$_{20}$ (BGO) and Bi$_{12}$SiO$_{20}$ (BSO) single crystals [2]. We found that when doped with transient metals or rare earth elements these crystals showed photochromic effect. It is known that the photochromic effect occurs in the solid state materials having the broad energy band: in the insulators and the materials at the boundary between insulators and semiconductors. The energy levels occurring as a result of the point defects presence (intrinsic or introduced by doping) are located within the forbidden energy band very deep under the conduction band or far above the valence band top. It means they have a specific properties, among others they are firmly located. The extraction or donation of a charge often results in the change of the energy level.

Among the inorganic photochromic materials, the following groups can be distinguished [1,3]:
1. Halides of alkaline metals,
2. Nitrides of alkaline metals,
3. Halides of rare earth,
4. Metal oxides,
5. Minerals.

The separate class of photochromic materials are photochromic glasses [4, 5]. Among them we can distinguish:
a. Impregnated porous glasses. They are obtained by impregnation of the porous glass having 30-100 A pores, using a photochromic liquid. The channels are then sealed so the colouring and decolouring can be repeated many times.
b. Glasses containing suspended in them some special crystallites. To this kind of systems belong aluminium silicon-br-natrium with molybdenum silver tungstate introduced and another phosphorous glasses containing thallium chloride crystallites.
c. Homogeneous glasses. Also in some homogeneous glasses photochromic effect can be seen. These effects usually appear under illumination by the high energy photons. To these glasses belong for instance lead sillicide glasses coloured with illumination by gamma rays and reduced alcaline silicite glasses doped with cerium and manganese oxides and coloured by UV illumination. The characteristic feature of these glasses is that excitation induced absorption spectra do not depend of dopants in a visible manner. The dopants however can enhance or reduce the effect and even completely eliminate it.

The photochromic effect in the crystals such as rare earth doped Ca F$_2$ or Na and Ca doped KCl as well as transient metal doped SiTiO$_3$ are discussed in Refs [6, 7]. The following processes occurring in inorganic solid state materials can be involved in photochromic effect:
1. The formation of the colour centres connected with the intrinsic and intentionally doped point defects as well as formation of their aggregates.
2. Processes connected with the impact of light on the dopants charge state (elements of rare earth and transient metals).
3. Processes connected with creation of the polarons of small trap dimensions on dopants and other defects.

Our studies on the sillenites BGO, BSO, BTO (T=Ti) and mixed BTMO (M=Pb) were connected with such effects as photorefraction, photochromizm and photoconduction. Undoped and intentionally doped sillenites show photochromic absorption described in the frame by the small polaron bound to a tetrahedrally located dopant (ie. Mn, Cu, Co) or a centre (of a similar structure) of the hole bound to a Bi^{3+} ion also tetrahedrally located. In the majority of known cases of photochromizm in the crystalline insulators the processes of the charge transfer between at least two centres occurs through the bands. This shows that the photoconductance effect should be present. The centre responsible for photochromic absorption is localized in deep state but the centre involved in photochromic effect in sillenites are electron trap states which are rather shallow. In this paper we present the results of our studies of photochromic effect in the doped sillenites BGO, BSO, BTO and BTMO.

2. Technology and the study results

All the sillenite single crystals were investigated in our laboratory starting with growing them by the Czochralski or high temperature solution growth method. Details of the technology were presented among others in our papers [7-10]. The spectroscopic measurements set is shown in Fig. 1. It consists of the light source, monochromator and detection system. There were used different prisms or diffraction grids and detection units depending on the wavelength.

The measurements were carried out in a wide range of temperature from 1.1 K up to 500 K. The appropriate cryogenic systems were used to perform the measurements in the low and higher temperature range. The system has been constructed in our laboratory. Cryostat has two types of windows: CaF$_2$ and synthetic quartz. Vacuum pump was applied in order to obtain temperatures as low as 1.3 K. Reducing the heating of the sample caused by the measurement light we obtained the temperature as low as 1.1 K.

Optical and photochromic absorption measurements were carried out within a wide spectral range 4000-30000 cm^{-1}. To achieve this, there was need to use three different sets, among them one with two monochromators deflecting the stimulating beam of light.

Optical measurements were performed using the phase sensitive method by Lock-In Amplifier 5200 model from the Princeton Applied Research (the mechanical modulator was used to modulate the light). The system operation was controlled by the computer program TestPoint from Keithley firm. Fig. 1 presents the whole system.

3. Experimental results of photochromic effect of doped BGO and BSO single crystals

During seventieth of the last century we performed the studies on photochromic absorption in BGO and BSO single crystals doped mainly with transient metal elements (Mn, Cr and Co). Wardzyński, Łukaszewicz and Żmija were first to publish in 1979 [2] in Optical Communication the study results on photochromic effect in these materials.
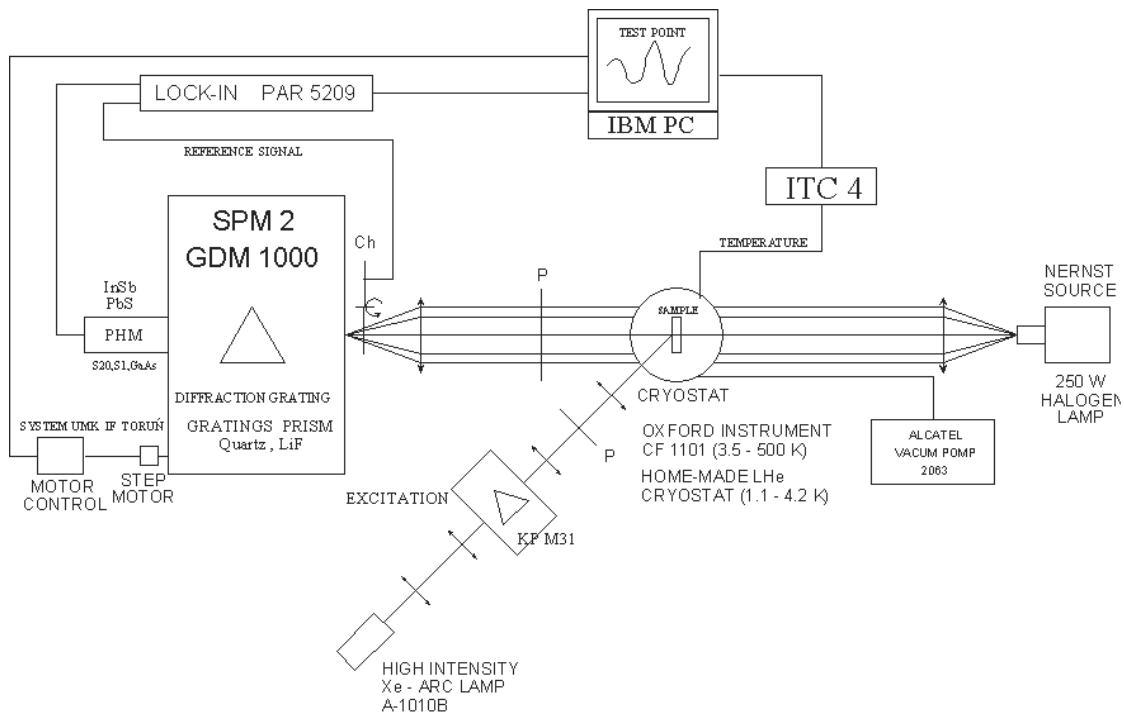
Fig. 1. The luminescence measurements set at low temperatures

In Fig. 2 the study results of absorption in BGO:Cr single crystals at room temperature are presented. Curve A shows absorption before illumination, while curve B – after illumination. We can see the increase of absorption illumination in the range of 12000-15000 cm^{-1}, that lies in the red part of the spectrum. The spectrum of the light inducing the coloration change is presented in Fig. 3 (curve A). Light of the wave numbers larger than 13000 cm^{-1} was found to be active in the coloration process which lies in the area of shorter wavelengths than the area where as a result of illumination the absorption changes occur (curve A). Curve B in Fig. 3 presents the spectrum of the light which is able to decolourate the sample which was previously coloured by illumination. Fig. 4 shows the absorption spectrum in BGO:Cr at liquid helium temperature. As can be seen the spectra in this temperature and at room temperature are similar. The absorption spectra of BGO:Mn single crystals before and after illumination are shown in Fig. 5 at room temperature and in Fig. 6 the same at liquid helium temperature. The absorption spectra of BGO and BSO single crystals doped with the same elements were found to be very similar.
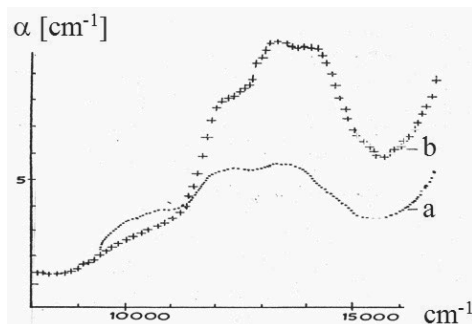

Fig. 2. Absorption spectrum of BGO:Cr single crystals at room temperature; a - absorption before illumination, b – after illumination
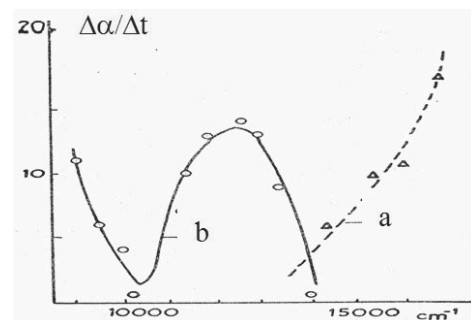

Fig. 3. a - the spectrum of the light inducing the coloration change. b - the spectrum of the light which is able to decolourate the sample which was previously coloured by illumination
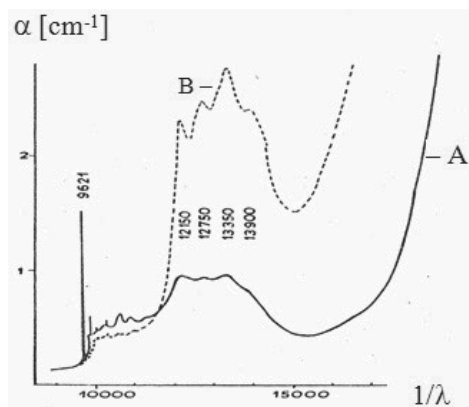
Fig. 4. Absorption spectrum of BGO:Cr at liquid helium temperature. A – before illumination, B – after illumination
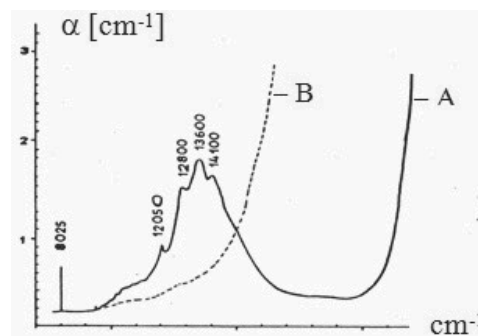

Fig. 6. The absorption spectra of BGO:Mn single crystals before and after illumination at liquid helium temperature
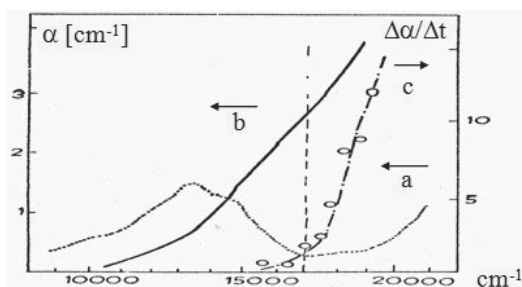

Fig. 5. Absorption spectrum of BGO:Mn, at liquid helium temperature. a – before illumination, b – after illumination, c – the rate of changes of absorption at 17000 cm^{-1} during illumination

Understanding of physical processes in the transient metal elements doped BGO and BSO single crystals requires the knowledge about their charge state. The measurements of the paramagnetic resonance spectrum was found to be very helpful in receiving the useful answers about the surroundings of the dopant and their charge state. We found [11] that in the case of BGO and BSO single crystals the doping elements of transient metal replace the be connected with the change in their charge state by one germanium (silicon) atoms. The photochromic effect should be connected with the change in their charge state by one electron ie. $Mn^{+4} \rightarrow Mn^{+5}$ and $Cr^{+3} \rightarrow Cr^{+4}$. Fig. 7 shows the proposed schematic presentation of the energetic levels obtained on the basis of the above remarks. The absorption in Mn^{+4} ion results in the transition of the electron to the conduction band. Then the electron is trapped in the electron trap. Before the illumination both Mn^{+4} and Mn^{+5} centres exist. However, after illumination almost all Mn^{+4} centres are transferred to the Mn^{+5} state. The similar model was proposed for the case of BGO:Cr, here we have $Cr^{+3} \rightarrow Cr^{+4}$ transition.
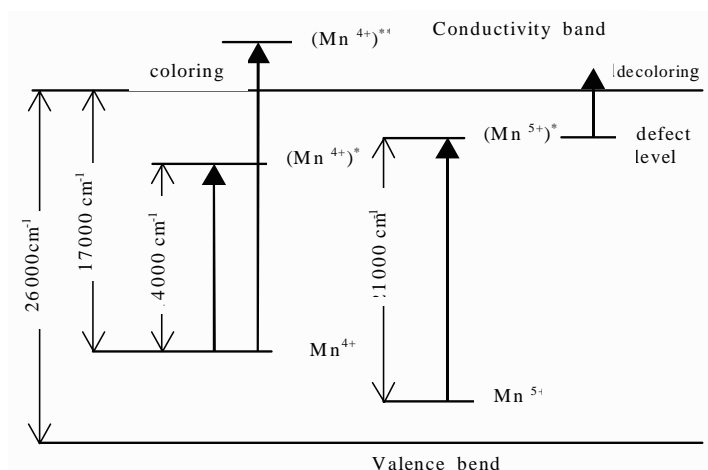

Fig. 7. The proposed schematic presentation of the energetic levels obtained on the basis of the investigations on BGO:Mn single crystal

4. Investigation results of optical properties of mixed sillenite single crystals (absorption and photochromic absorption)

Photochromic effect of mixed $Bi_{12}Ti_{1-x}Pb_xO_{20}$ (BTPbO) sillenite single crystals at temperature in the range 3.5-500 K and spectral range UV-VIS-NIR have been investigated [8, 9, 10, 12]. Uncoloured state was achieved by annealing of the crystal in darkness at high temperature (in the case of these crystals it was 520 K). The coloured state of the sample means the state after illumination at given temperature. The coloured spectrum for BTPbO was found to occur for the shorter wavelengths than about 600 nm. The spectral distribution of the absorption at the coloured state only little depends on the colouring light wavelength, however, the intensity of all absorption bands depends on the colouring light wavelength.

In the case of BTPbO sample with x=0.3, Figs. 8 and 9 present the typical absorption spectra as a function of temperature in uncoloured and coloured states, respectively (illumination with blue light). The absorption spectra consist of bands which are determined by extraction the uncoloured spectrum from the coloured one. The absorption bands are associated with the polaron bound to the ion localized tetrahedrally [13] or to the analogous centre Bi^{+3+h} [14]. Some BTPbO single crystals show the so called gray.

The Spectra shown in Figs. 9 and 10 compose of few bands, the location of which are determined by analyzing the photochromic absorption of BTPbO (x=0.35) as a function of temperature which is shown in Fig. 10. Fig. 11 presents the so called photochromic effect thermal stability curve for BTPbO (x=0.5) single crystal. This kind of curves show the photochromic changes for selected wavelength which corresponds to the changes in concentration of the centre in the defined charge state.
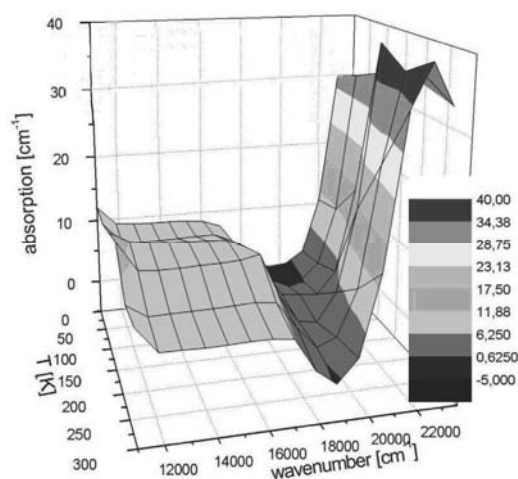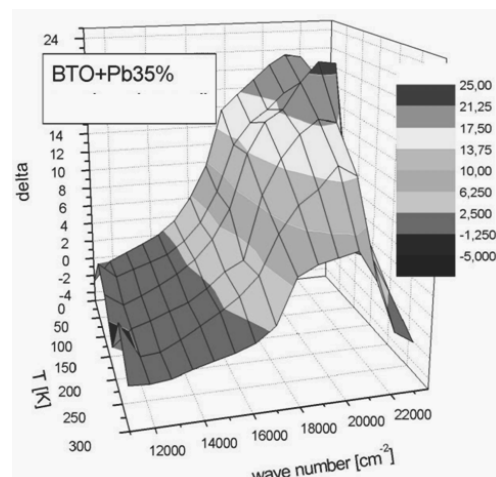

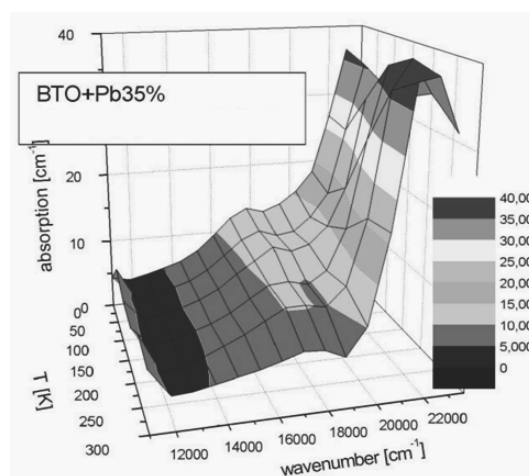Fig. 9. Absorption spectra as a function of temperature in coloured state for BTPb$_X$O sample with x=0.35

Fig. 10. Spectrum of photochromic absorption of BTPb$_X$O (x=0.35) as a function of temperature

Table 1.
Parameters of thermal decolouration curves

	T_0 [K]	ΔE [cm^{-1}]
BTO+Pb35%	412.16	6475.96
BTO+Pb35%	398.61	8252.20
BTO+Pb50%	418.03	5030.76
BTO+Pb65%	396.99	4127.57
BTO+Pb80%	373.70	3267.51

Table 1 presents the parameters of the thermal stability curves. The characteristic temperature gives the temperature at which the thermal decolouration process plays a significant role. The second parameter gives the ionization energy (thermal) of a trap responsible for the thermal stability of the photochromic changes [8]. As can be seen these changes are irregular as a function of concentration which corresponds to the qualitative changes in the atomic structure [12].
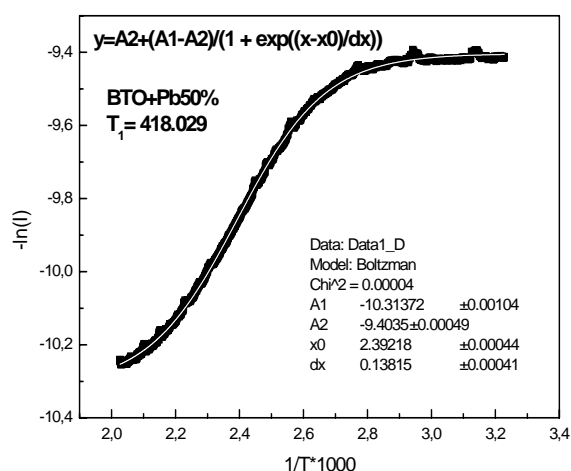

Fig. 8. Absorption spectra as a function of temperature in uncoloured state for BTPb$_X$O sample with x=0.35

Fig. 11. The photochromic effect, thermal stability curve for BTPbO (x=0.35) single crystal

5. Summary

The photochromic effect is a reversible process of absorption changes in some materials induced by illumination. The changes can be removed and the absorption can be brought into its initial value by means of illumination as well as by annealing. In this paper the special attention has been devoted to the single crystals such as $Bi_{12}GeO_{20}$ (BGO), $Bi_{12}SiO_{20}$ (BSO) and BTPbO doped with transition or rare earth metals. We describe the measurement methods and instrumentation connected with this effect and the selected basic absorption spectra of the investigated single crystals enabling to understand some features of the photochromic effect occurring in these crystals. The attached some selected curves provide the valuable information concerning the physical phenomena involved in colouring and decolouring processes in these single crystals. We found that in the case of BGO and BSO single crystals the doping elements of transient metal replace the germanium (silicon) atoms. The photochromic effect should be connected with the change in their charge state by one electron ie. $Mn^{+4} \rightarrow Mn^{+5}$ and $Cr^{+3} \rightarrow Cr^{+4}$. We also propose the schematic presentation of the energetic levels obtained on the basis of the above remarks. The absorption in Mn^{+4} ion results in the transition of the electron to the conduction band. Before the illumination both Mn^{+4} and Mn^{+5} centres exist. However, after illumination almost all Mn^{+4} centres are transferred to the Mn^{+5} state. The similar model was proposed for the case of BGO:Cr, here we have transition $Cr^{+3} - Cr^{+4}$.

In the case of BTPbO mixed crystals, the absorption bands are associated with the polaron bound to the ion localized tetrahedrally [15] or to the analogous centre Bi^{+3+h}. Some BTPbO single crystals show the so called gray spectrum. This kind of spectrum is likely to consist of many other almost identical bands located closely to each other and each of them corresponds to a single local centre which is bound to a lead ion and is modified by the structural changes (vacancies).

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