

Electrical and optical properties of glasses based on TeO_2 - Sb_2O_3 - PbCl_2

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There were investigated optical transmittance and direct electrical conductivity of the glass systems of TeO_2 - Sb_2O_3 - PbCl_2 . Optical transmittance measured in the wave range of (2.5 – 7.5) μm depends significantly on the amount and the nature of defects of glasses and the glass composition. The highest value of optical transmittance was found for glass of the composition of 40 TeO_2 - 10 Sb_2O_3 - 50 PbCl_2 . Direct electrical conductivity in the temperature range of (20 – 240) °C has the constant value of activation energy (~ 1.1 eV) if glasses own the low concentration of PbCl_2 . If the concentration of PbCl_2 is increased then the change of value of activation energy at the temperature ~ 80°C was observed. The values of conductivity of the system TeO_2 - Sb_2O_3 - PbCl_2 are strongly affected by the concentration of PbCl_2 .

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1. Introduction

The intensive development of the new applications utilizing the elements working in the infrared range of spectrum forces to orientate itself to find and search new materials. Especially glasses based on heavy metal oxides are very perspective for optical application in the range of the wavelengths up to 8 μm [1, 2]. Their preparation is quiet exacting; it requires consistent monitoring of its individual stages. There is important to decrease defects (bubbles and crystals) as well as OH group impurity concentration, what increases significantly the glass tendency to crystallize and it makes at the same time worse optical properties as the value of absorption is rising. Further physical properties are observing, too. These would be utilized to control the individual stages of glass preparation of searched systems [3,4].

2. Experimental

The searched glasses of the system TeO_2 - Sb_2O_3 - PbCl_2 were prepared by means of PbCl_2 , Sb_2O_3 and TeO_2 of the purity of 99.9 %. The mixture was inserted to the quartz crucible after its homogenisation. Melting was very rapid up to 5 minutes usually, with respect to the low viscosity of the melt. The elongated shape of the open crucible ensured restricted access of the surrounding atmosphere. Casting was performed to the brass forms. The glasses were tempered at temperature of glass transformation from 30 minutes to 1 hour after the casting. Consequently glasses were annealed to the room temperature by cooling rate 1 °C/min. The medium over the melting was change in the case of 70 TeO_2 -10 Sb_2O_3 -20 PbCl_2 glass. There were used vacuum (V607), gases N_2 (V603), O_2 (V604) and the mixture Cl_2/O_2 (V605). The list of samples is plotted in Table 1 together with their marks later used in text and Figs.

Table 1. List of samples, their composition, microscope picture and temperature to glass transition.

Mark	Change	Composition [mol%]			Microscope picture	T_g [°C]
		Sb_2O_3	PbCl_2	TeO_2		
V501	Composition	-	20	80	It contains bubbles and crystals	275
V706		-	40	60	Clean glass containing a few crystals	235
V504		10	10	80	Clean sample	290
V511		10	30	60	It contains small starry crystals and a little bubbles, too	250
V409		10	40	50	It contains bubbles and crystals rarely	235
V803		10	50	40	Clean glass containing a few small crystals	220
V701		20	20	60	Clean glass containing a few textured bubbles	265
V805		20	30	50	Very clean glass contains small starry crystals	255
V505		10	20	70	Clean glass containing a few small crystals	275
V607		Preparation	10	20	70	A lot of bubbles, somewhere random formations
V603	10		20	70	Clean sample	275
V604	10		20	70	Clean sample	275
V605	10		20	70	Clean sample	275

Samples for measurements of electrical and dielectrical properties (diameter of 9 mm, thickness about 2 mm) were coated by the conductive layer on the contact surfaces. The temperature dependency of direct electrical conductivity (when the rate of heating was 5 °C/min) was measured by direct method of the monitoring of current flowing through the sample when voltage was constant. The value of current was determined by Keithley device [5, 6]. The optical transmittance was determined by means of Perkin Elmer Spectrum BX device. Microscope working in the range of optical waves was utilized for the sample detection. Temperature T_g (Table 1) was determined by DSC (Seiko DSC 220) device.

Direct electrical conductivity presents the competence of the charge particles to move by ordered motion in the large distance comparing the nuclei dimensions. It is affected by temperature and the measured results could be relatively suitable described by Arrhenius relation [7]

$$\sigma = \sigma_0 e^{-\frac{U}{kT}} \quad (1)$$

where σ is direct electrical conductivity, U is the total activation energy needed to the creation and the motion of the free charge carrier, k is Boltzmann constant, T is thermo-dynamical temperature a σ_0 is pre-exponential factor. In general we can exploit for in-ordered systems (glasses, ceramics, etc.) the same physical methods as for crystal materials. It means to use modified relations and conceptions about the charge carriers migration in the in-ordered net [8].

3. Results

Temperature dependencies of σ of the measured glasses depend markedly on the concentration of individual compounds of the glass system (Fig.1). The measured values of σ increase with PbCl_2 concentration. The activation energy when the concentration of PbCl_2 is low is not changing strongly (Fig.2). There is detectable decrease of the activation energy, if the concentration of PbCl_2 is rather higher. The sharp change of U is at temperature about 80 °C when the concentration of PbCl_2 is high.

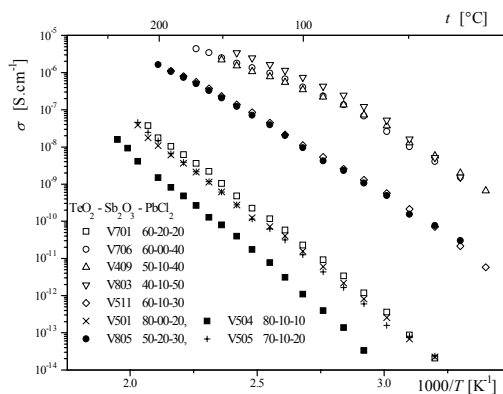


Fig.1. Temperature dependencies of direct electrical conductivity σ of TeO_2 - Sb_2O_3 - PbCl_2 glass system.

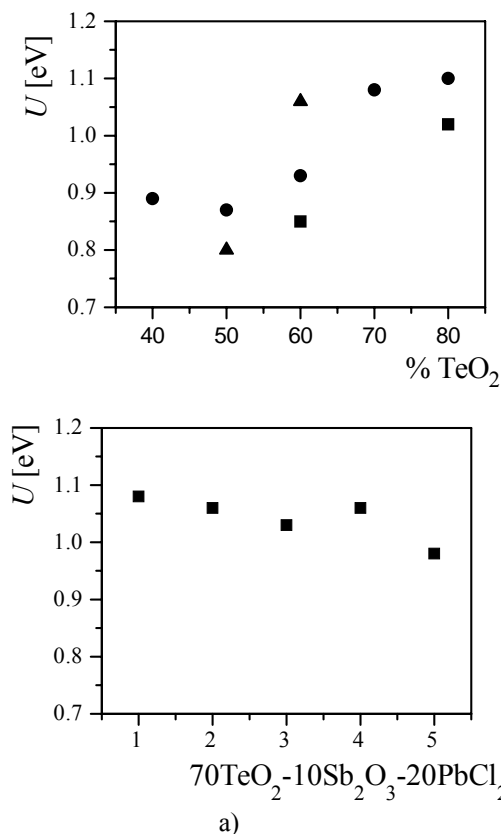


Fig. 2. Dependency of measured values of activation energy U determined from σ measurements when temperature is increased up to 80°C: a) The change of composition of glass system TeO_2 - Sb_2O_3 - PbCl_2 : ■ 0% Sb_2O_3 , ● 10% Sb_2O_3 , ▲ 20% Sb_2O_3 . b) The change of technology of preparation of glass system 70TeO_2 - $10\text{Sb}_2\text{O}_3$ - 20PbCl_2 : (1) V505, (2) V607 vacuum, (3) V603 N_2 , (4) V604 O_2 , (5) V605 Cl_2/O_2 .

The change of the used technology of the preparation (various medium during the melting) of 70TeO_2 - $10\text{Sb}_2\text{O}_3$ - 20PbCl_2 glass causes the significant change of electrical properties, similarly as its composition. The measured values of σ are nearly equal (Fig. 3) and also associated activation energy U (Fig. 2b). Slow change is in the case of glass created in the mixed medium Cl_2/O_2 only.

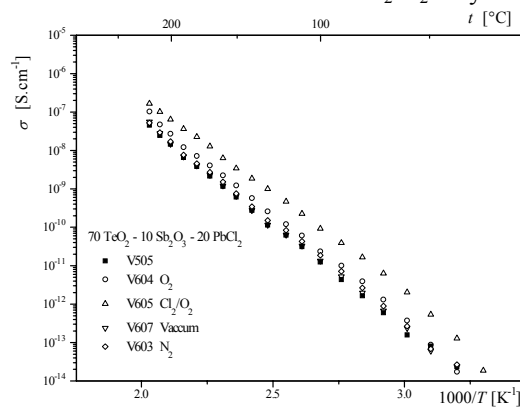


Fig. 3. Temperature dependencies of direct electrical conductivity σ of glass system of TeO_2 - Sb_2O_3 - PbCl_2 of the various preparation technology.

Comparing the measured values of σ (Fig. 4) and the values of T_g (Fig. 5) one can find the significant correlation. When the content of PbCl_2 in the volume of glass is higher, the found out values of σ are increasing, too, and the values of T_g are decreasing.

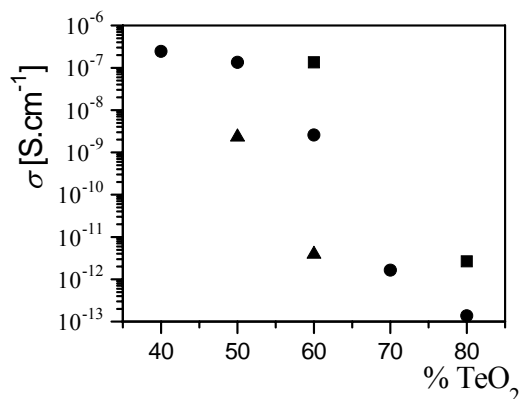


Fig. 4. Dependency of the measured values of direct electrical conductivity σ at temperature of 80°C depending on the composition of glass $\text{TeO}_2 - \text{Sb}_2\text{O}_3 - \text{PbCl}_2$: ■ 0% Sb_2O_3 , ● 10% Sb_2O_3 , ▲ 20% Sb_2O_3 .

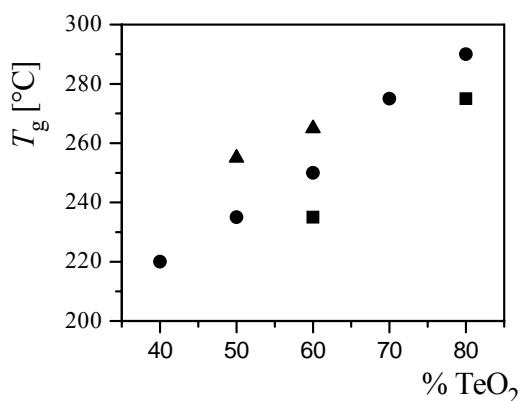


Fig. 5. Dependency of the measured values of temperature of T_g depending on the composition of glass $\text{TeO}_2 - \text{Sb}_2\text{O}_3 - \text{PbCl}_2$: ■ 0% Sb_2O_3 , ● 10% Sb_2O_3 , ▲ 20% Sb_2O_3 .

Optical properties of the searched glasses are affected significantly by their composition (Fig. 6), too. In general the values of optical transmittance T are increasing when the content of PbCl_2 is growing. The high absorption caused by OH groups ($\sim 3 \mu\text{m}$) is opened. The highest values of T were found out measuring the glass samples $40 \text{ TeO}_2 - 10 \text{ Sb}_2\text{O}_3 - 50 \text{ PbCl}_2$. The various medium used during melting affected markedly the values of T . All used media (N_2 , O_2 , O_2/Cl_2) cause the better optical properties of $70 \text{ TeO}_2 - 10 \text{ Sb}_2\text{O}_3 - 20 \text{ PbCl}_2$ glass. The opposite effect was found using vacuum over the heated mixture.

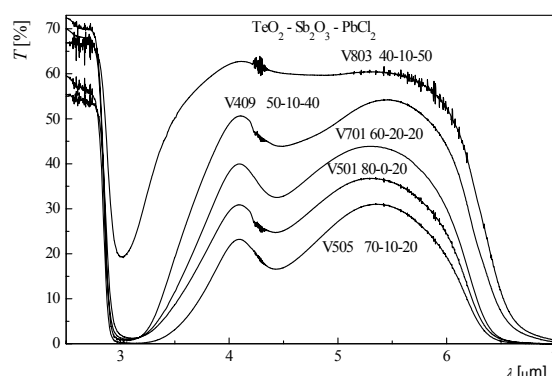


Fig. 6. Transmittance T of $\text{TeO}_2 - \text{Sb}_2\text{O}_3 - \text{PbCl}_2$ glass of the various compositions.

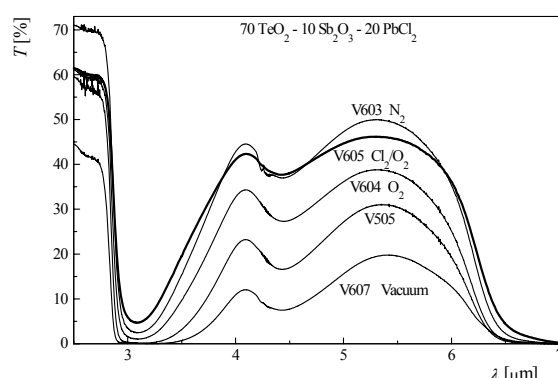


Fig. 7. Transmittance T of $70 \text{ TeO}_2 - 10 \text{ Sb}_2\text{O}_3 - 20 \text{ PbCl}_2$ glass prepared by the various technology.

4. Discussion

The measured values of σ of the researched $\text{TeO}_2 - \text{Sb}_2\text{O}_3 - \text{PbCl}_2$ glasses are affected considerable by their composition. Their electrical properties very slowly respond to the changes of technology oriented to eliminate OH groups. It is very interesting result as the concentration of OH groups usually correlated significantly with the electrical properties of heavy oxides glasses [8, 9]. Optical properties are to the concentration changes more sensitive. The influence of the medium used during the melting for the preclusion of the contamination by OH groups (Fig. 7) is registered. The glasses are characterized by lower values of absorption at $\sim 3 \mu\text{m}$ using these media.

The content of (crystals and bubbles) has the negligible influence on the measured properties of glasses. It is affected by their very low volume proportion because crystalline phase causes namely electrical properties glasses, usually [10, 11].

However there are searched those properties of $\text{TeO}_2 - \text{Sb}_2\text{O}_3 - \text{PbCl}_2$ glass system which are affected by the PbCl_2 content. If the PbCl_2 concentration increases the values of direct electrical conductivity increases, too, but the activation energy decreases. It is the behaviour of typical modifier of the glass net. Increasing its presence

the concentration of defects supporting the increase of the electrical conductivity values growths, too.

The important fact is the reality that that influence is given by chloride form especially, because the chlorine concentration affects optical properties markedly. The reduction of its concentration is reflected by the decreasing of the values of transmittance (Fig. 7). This is the reason why we can register slow increase of the electrical conductivity values (Fig. 3) while the protecting medium Cl_2/O_2 was utilized during the smelting.

5. Conclusions

We can summarize that direct electrical conductivity and transmittance of the chosen glasses of $\text{TeO}_2 - \text{Sb}_2\text{O}_3 - \text{PbCl}_2$ system are affected by the PbCl_2 concentration. Its stabilization in the glass volume and the low OH content are dominant to reach the required optical glass properties. Glass 40 $\text{TeO}_2 - 10 \text{Sb}_2\text{O}_3 - 50 \text{PbCl}_2$ was found out for the reached optical properties as prospective for the applications mentioned in the introduction.

The presented result were gained cooperating search activities of Department of Non-metallic Materials of the Faculty of Materials Science and Technology of the Slovak university of Technology in Trnava (Slovak Republic), Laboratory of Inorganic Materials, Institute of Inorganic Chemistry of Academy of Science of Czech Republic in Prague (Czech Republic) and Laboratoire des Matériaux Photoniques, Centre d' Etudes des Matériaux Avancés, Université de Rennes, Rennes, (France) supported by projects VEGA 1/2077/05, APVV-20-043505, the project 104/05/0878 of Czech Republic and international project SK-FR-00106.

References

- [1] D. W. Hewak, R. C. Moore, T. Schweizer, J. Wang, B. Samson, W. S. Brochlesly, D. N. Payne: Proceedings of 10th Int. Symposium on Non-oxide glasses, Corning, USA (1996), 157.
- [2] D. Ležal, J. Pedlíková, M. Poulain: Proceedings of SPIE - Infrared Glass Optical Fibers and Their Applications, Int. Soc. Opt. Eng., vol 34161043 Quebec 1998.
- [3] D. Ležal, J. Pedlíková, M. Karel, J. Zavadil, O. Procházková, J. Kalužný, E. Mariani: Telluride and related heavy metal oxide glasses: preparation and properties. In: 13th International scientific conference „CO-MAT-TECH 2005“, MtF STU Trnava, Trnava 2005, p. 728 – 735. ISBN: 80-227-2286-3.
- [4] J. Pedlíková, J. Zavadil, O. Procházková, J. Kalužný: Preparation and characterization of TeO_2 based glasses. Materials science forum. Vols. 480-481 (2005) pp. 315-322. online at <http://www.scientific.net>.
- [5] M. Kubliha, R. Čička: The principles of modulus and impedance spectroscopy and the application in investigation of defects and structural changes in non-ordered structures. In: Materials Science and Technology, ročník 6, číslo 2, 2004. Materiálovotechnologická fakulta STU v Trnave. ISSN 1335-9053. <http://web.mtf.stuba.sk/sk/casopis/archiv/2006/2/kubliha.pdf>
- [6] R. Čička, V. Trnovcová, M. Yu. Starostin: Electrical properties of alumina-zirconia eutectic composites. In: Solid State Ionics 148 (2002) 425-429.
- [7] A. B. Lidiard: Handbuch der Physik. Vol. XX. Berlin 1957, p.246.
- [8] J. Kalužný, D. Ležal, M. Kubliha, E. Mariani, T. Kozík, J. Pedlíková, P. Kostka: Electrical and optical properties correlation of special glasses. 13. International symposium of non-oxide glasses and new optical glasses. September 9-13, 2002, Pardubice, Czech Republic, University of Pardubice, part I, p.607-610. ISBN 80-7194-461-0.
- [9] J. Kalužný, D. Ležal, J. Pedlíková, M. Kubliha, V. Labaš, J. Zavadil, E. Mariani: Electrical, dielectric and optical properties of $\text{TeO}_2\text{-PbCl}_2\text{-PbF}_2$ glass systems. Journal of Optoelectronics and Advanced Materials Vol. 7, No. 5, October 2005, p. 2309 – 2315. Online in: <http://inoe.inoe.ro/JOAM/>.
- [10] M. Kubliha: Structural defects of glasses based on Sb_2O_3 . In: Zborník prednášok zo 10. vedeckej medzinárodnej konferencie „Akademická Dubnica 2004“, 2004, Dubnica nad Váhom, MtF STU Trnava, s.295-298. ISBN 80-227-2076-3
- [11] M. Kubliha: Investigation of structural changes and defects of glasses based on Sb_2O_3 by means of electric methods. In: XVI. Medzinárodná vedecko-odborná konferencie „DIDMATTECH 2003“. PdF UP Olomouc, Votobia Praha 2003, s.101-104. ISBN 80-7220-150-6.

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