Bulgarian Chemical Communications, Volume 49, Special Issue A (pp. 103–109) 2017

Influence of TiO_2 on the thermal stability and crystallization of glasses within $TeO_2 – Bi_2O_3 – Nb_2O_5 – ZnO$ system

Sv. Ganev[1], S. Parvanov[1], S. Slavov[1], A. Bachvarova-Nedelcheva[2]*, R. Iordanova[2], Y. Dimitriev[1]

[1] *University of Chemical Technology and Metallurgy – Sofia, "Kl. Ohridski" blvd. 8, 1756 Sofia, Bulgaria*
[2] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev" str., bld. 11, 1113 Sofia, Bulgaria*

Received October, 2016; Revised December, 2016

In this study we selected the $TeO_2 – Bi_2O_3 – Nb_2O_5 – ZnO$ system. The investigation covers TeO_2 – based glasses containing Nb_2O_5 and Bi_2O_3 up to 10 mol%, ZnO from 5 to 10 mol%, while the TiO_2 varies from 5 to 50 mol%. The obtained glasses were transparent and yellow colored (TiO_2 up to 20 mol%). The thermal stability of the samples was determined by DTA using the difference ΔT between exothermic peak of crystallization (T_x) and that for glass transition temperature Tg (ΔT = 50–115 °C). Several crystalline phases were identified by XRD, between them more important are $ZnTeO_3$ and $TiTe_3O_8$ (in compositions above 20 mol% TiO_2) due to their good dielectric properties. The analysis of spectra shows that network of glasses consist mainly of TeO_4 (TBP) units. The preliminary electrical measurements showed that the samples are with low conductivity and there is no significant change of the dielectric losses up to 600 °C. The as-prepared crystalline samples are with low conductivity and good dielectric properties.

Keywords: glass-ceramics, thermal stability, structure, properties.

INTRODUCTION

Currently intensive search is going onto find dielectric materials for Low Temperature Cofired Ceramics (LTCC) technology, that are applicable in wireless communications and broadcasting industry. In the last years as a preferred method for preparation of ferro-electrics materials was used melt quenching and crystallization from glasses (glass-ceramics) [1]. The tellurite glass materials as a matrix are very suitable due to low melting temperature, chemical resistance, good dielectric properties and good solubility of heavy metal ions [2]. Up to now several three-component systems with the participation of Nb_2O_5, TeO_2, Bi_2O_3, ZnO have been studied. Glasses in the $TeO_2 – Nb_2O_5 – Bi_2O_3$ system [3] were characterized with good thermal stability and Tg of glasses are in the range 387–439 °C for compositions containing 85–90 mol% TeO_2. In the last investigation concerning the structure of glasses in the same system [4] was stated the formation of "anti-glass spherolites" and the short range order of glasses was determined by the high energy x-ray diffraction. In the $TeO – Nb_2O_5 – ZnO$ system [5] glasses have been obtained in the range 5–25% ZnO. In a four component glass composition $75TeO_2 – 10Bi_2O_3 – 10Nb_2O_5 – 5ZnO$ was established that introduction of Er^{3+} is suitable for laser materials [6]. In a system with participation of TiO_2 [7] was shown that Bi_2O_3 and TiO_2 influence the glass transition temperature (Tg). Titania (TiO_2) keeps the polymerized structure while Bi_2O_3 destroys the glass network. On the other hand, it was shown that TiO_2 [8] was effective nucleation agent to promote the three dimensional crystallization in $TeO_2 – Bi_2O_3 – Nb_2O_5$ system. Another interesting fact is that heat treatment in oxygen flow (solid state reaction or melting) leads to oxidation and formation of tellurites [9]. It was found that compositions in the $Bi_2O_3 – TiO_2 – TeO_2$ system crystallized as three-component compounds containing Te^{6+} ions. It was also established that these compounds possess good microwave dielectric properties. The above pointed results additionally motivated us to orientate our research toward tellurite glasses.

The purpose of this paper is to study the influence of TiO_2 on the thermal stability and crystallization of selected glasses within the $TeO_2 – Bi_2O_3 – Nb_2O_5 – ZnO$ system.

* To whom all correspondence should be sent:
E-mail: albenadb@svr.igic.bas.bg

EXPERIMENTAL

Samples preparation

All specimens are shown in Table 1. The batches were prepared using reagent grade TiO_2, TeO_2, Bi_2O_3, Nb_2O_5 and ZnO. They were homogenized of about 10 grams and were melted in air for 20–30 mins using silica crucibles at temperatures between 800–1100 °C. The melting temperature was selected depending on composition. Compositions containing higher TiO_2 (40 mol% – sample 6J and 50 mol% – sample 6K) content were melted at 1100 °C. The glass forming ability of the compositions was determined by pouring of the melts between two copper plates at cooling rate 10^1–10^2 K/s. The obtained glasses were transparent and yellow colored (samples containing up to 20 mol% TiO_2).

Samples characterization

The phase formation of the powdered samples was established by X-ray phase analysis with a Bruker D8 Advance diffractometer, using CuKα radiation in the 10 < 2theta < 80 range. The differential thermal analysis (DTA) of selected compositions was carried out on STA PT1600 with Pt/Pt/Rh thermocouples with a heating rate of 10 K/s in air flow, using Al_2O_3 as a reference material. The thermal stability of the samples was evaluated using the difference ΔT between exothermic effect of crystallization (T_x) and that for glass transition temperature Tg (ΔT = Tx – Tg). The IR spectra of the glasses were recorded in the 1400–400 cm^{-1} region using the KBr pellet technique (Nicolet-320 FTIR spectrometer). The optical spectra of selected powder samples at room temperature were recorded with a spectrometer (Evolution 300 UV-Vis Spectrophotometer) employing the integration sphere diffuse reflectance attachment. The samples were measured in the wavelength (λ) range of 200–800 nm with a magnesium oxide reflectance standard used as the baseline. The uncertainty in the observed wavelength is about ±1 nm. The Kubelka – Munk function (F(R∞)) was calculated from the UV–Vis diffuse reflectance spectra. Measurements of the electrical conductivity and dielectric losses of selected samples are performed by LCR Meter MS5308 (Shenzhen Master Industrial) with frequency of 1 kHz using two-terminal method with graphite electrodes.

RESULTS AND DISCUSSION

Phase characterization and thermal stability

The XRD patterns of investigated samples are shown in Fig. 1 (a, b, c, d, e, f) and Table 1 summarized the detected by XRD method main crystalline phases. As it is seen from the figure, both samples containing 5 and 10 mol % TiO_2 (samples 6D – $5TiO_2.72TeO_2.5ZnO.9Bi_2O_3.9Nb_2O_5$ and 6C – $10TiO_2.60TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$) are amorphous. The increasing of TiO_2 content (20 mol%, sample 6E) led to partial crystallization and appearance of three crystalline phases $TiTe_3O_8$ (JCPDS 24-1348), TeO_2 (JCPDS 52-0795) and TiO_2 (rutile,

Table 1. Detected by XRD crystalline phases and observed by DTA effects in all investigated samples

Sample (abbrev.)	Compositions	Detected crystalline phases by XRD	Observed by DTA effects		
		1100 °C (20 mins)	Tg, °C	Tx, °C	DT = Tx – Tg
6K	$50TiO_2.20TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$	crystals $ZnTeO_3$ + Rutile (TiO_2) + $TiTe_3O_8$	–	–	–
6J	$40TiO_2.30TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$	glass + crystals $TiTe_3O_8$ + TeO_2 + (TiO_2) Rutile + $ZnTeO_3$	–	–	–
6I	$30TiO_2.40TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$	glass + crystals $TiTe_3O_8$ + TeO_2 + TiO_2 (Rutile)	–	–	–
6E	$20TiO_2.50TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$	glass + crystals $TiTe_3O_8$ + TeO_2 + TiO_2 (Rutile)	420	Tx_1 = 470 Tx_2 = 500	50
6C	$10TiO_2.60TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$	glass	355	Tx_1 = 470 Tx_2 = 550	115
6D	$5TiO_2.72TeO_2.5ZnO.9Bi_2O_3.9Nb_2O_5$	glass	380	Tx_1 = 480 Tx_2 = 530	100
VI – O	$80TeO_2.10Bi_2O_3.10Nb_2O_5$	glass	345	Tx_1 = 420 Tx_2 = 465	75

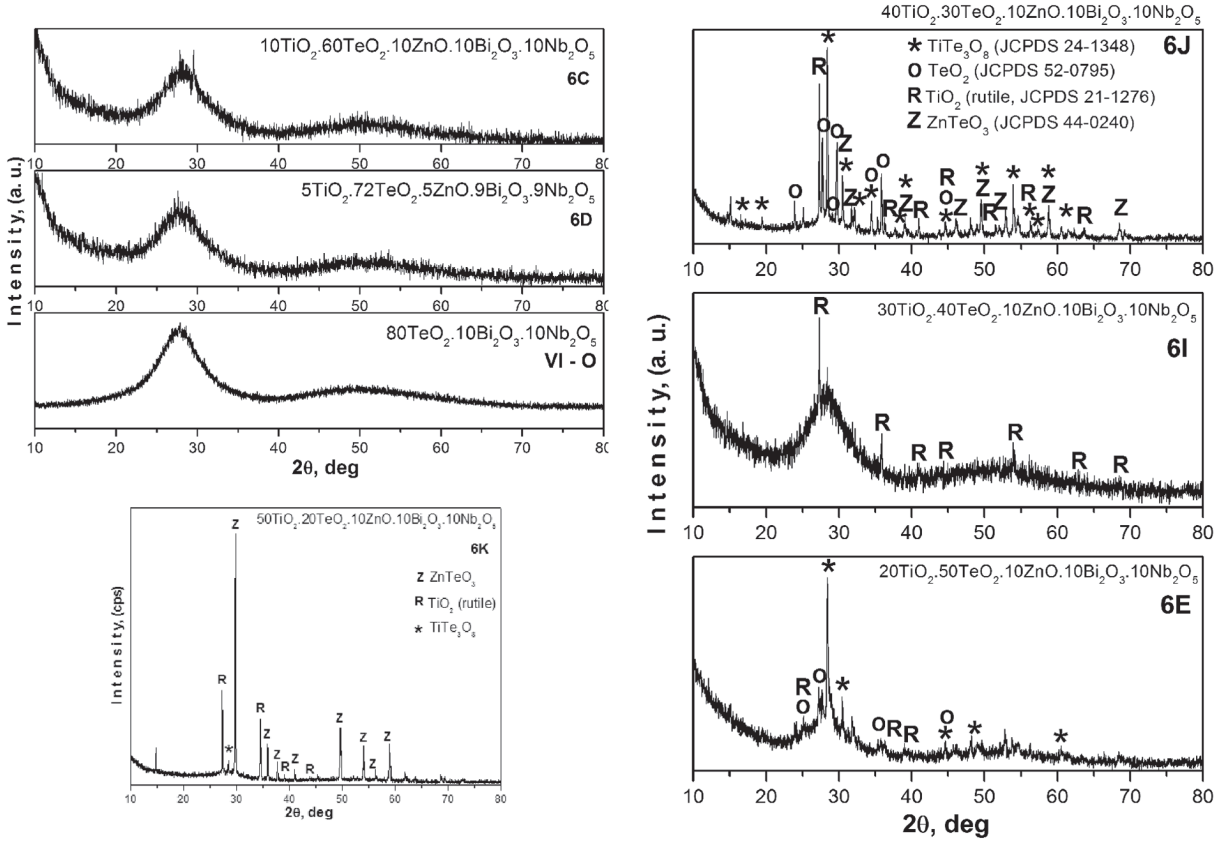

Fig. 1. XRD patterns of the obtained samples: $80TiO_2.10Bi_2O_3.10Nb_2O_5$ (VI-0), $5TiO_2.72TeO_2.5ZnO.9Bi_2O_3.9Nb_2O_5$ (6D); $10TiO_2.60TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$ (6C); $20TiO_2.50TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$ (6E); $30TiO_2.40TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$ (6I); $40TiO_2.30TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$ (6J); $50TiO_2.20TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$ (6K).

JCPDS 21-1276). At further increasing in TiO_2 content (30 mol%, sample 6I) the XRD pattern exhibited preserving of the amorphous phase along with simultaneous presence of TiO_2 (rutile) and $ZnTeO_3$ (JCPDS 44-0240). At 40 mol% TiO_2 all above pointed crystalline phases ($TiTe_3O_8$, TeO_2, rutile and $ZnTeO_3$) were detected. For sample 6K, containing highest TiO_2 amount (50 mol%) $TiTe_3O_8$, rutile and $ZnTeO_3$ were registered without TeO_2. Bearing in mind the obtained results, it could be summarized that addition of above 20 mol% TiO_2 stimulates the crystallization tendency of compositions.

The thermal parameters obtained from DTA curves of quenched samples are summarized in Table 1 and shown in Figure 2. They are characterized with the glass transition temperature (Tg) in the range of 345–378 °C and glass crystallization temperatures (Tx) above 400 °C. In all investigated samples two glass crystallization temperatures were observed related to the separation of two crystalline phases detected by XRD (Fig. 1a, b, c). The calculated $\Delta T = Tx - Tg$ was found to be in the range 50–115 °C that determines a good thermal stability

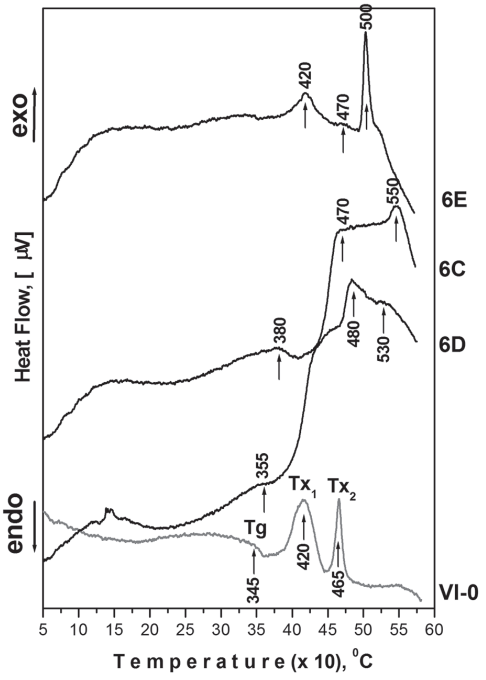

Fig. 2. DTA curves of selected samples VI-O, 6D, 6C and 6E.

of the investigated samples. A selected glass composition (6I) that is X-ray amorphous (Fig. 1b) was subjected to heat treatment at temperature near the glass crystallization temperature (500 °C) in order to identify the products of crystallization. Figure 3 presented the XRD result for sample 6I after 6 h heat treatment at 500 °C. The main crystalline phases TeO_2 and $TiTe_3O_8$ were detected which is different than the XRD result after the free cooling of the melt, where mainly TiO_2 (rutile) crystallized in the amorphous matrix (Fig. 1b).

IR and UV-Vis spectra

The IR spectra of investigated samples are shown in Fig. 4a, b. Two well resolved bands are observed with maxima near 630 and 470 cm^{-1}, as well as very small shoulder near 780 cm^{-1}. The assignment of the bands is made in the framework of the local point symmetry approaches following the methods developed by Nakamoto and Tart [10, 11]. Most of the compositions are with high tellurium dioxide content (50–80 mol%). That is why their spectra will be considered as that for tellurite systems. In amorphous state for tellurite compositions containing TeO_4 units, according our previous studies on tellurite glasses [12–15], the intensity of ν^{s}_{ax} at 635 cm^{-1} increases markedly instead of ν^{as}_{ax} and becomes a determining one. On one hand, $ZnTeO_3$ which contains distorted TeO_3 units [16, 17] is characterized by bands at 770, 700 and 670 cm^{-1}. As it was suggested in our previous studies, the observed bands are result from removal of the degeneracy of ν^{d} band of TeO_3 vibrations units with C_{3v} point symmetry [12]. On the other hand, $Zn_2Te_3O_8$ which contains two TeO_3^+ units connected with oneTeO_4 units [18] possesses three bands near 750, 685 and 555 cm^{-1} [10]. For the $TiTe_3O_8$ compound witch has cubic structure [19] the observed bands are at 770, 700 cm^{-1} and more intensive ones at 670 and 620 cm^{-1}. These bands are cubic for the cubic $TiTe_3O_8$ containing TeO_4 units [12, 20]. That is why the obtained results give us the reason to accept that the structure of the investigated glasses (short range order) is determined by TeO_4 units mainly (bands near 630 cm^{-1}). Probably they participated in the formation of bridging bonds Te–O–Te and Te–O–Ti. The influence of Nb_2O_5, Bi_2O_3 and ZnO is not discussed because their content is near than 10 mol%. Nevertheless, the intensive band around 470 cm^{-1}

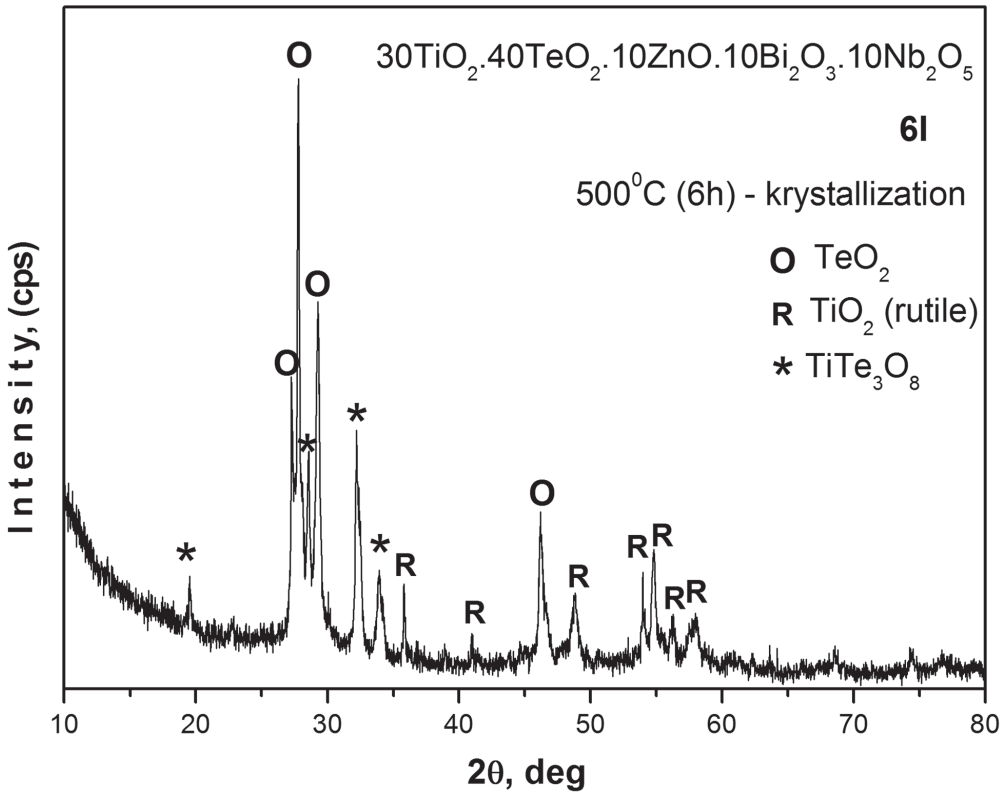

Fig. 3. XRD patterns of (a) $30TiO_2.40TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$ (6I) parent sample; (b) sample, heat treated at 600 °C for 5 h.

which obviously is a complex one, is due probably to the vibrations of different building units, such as TiO_6, BiO_n and ZnO_n [20]. In this spectral region are also the symmetric vibrations of the Te–O–Te bridges connecting different tellurite complexes.

The UV-Vis spectrum of a representative composition containing 30 mol% TiO_2 (6I) is shown in Fig. 5. It exhibits two weak absorption maxima at 255 and 260 nm and a stronger one at 330 nm. It is well known that the transitional metal oxides with d^o electron configuration give absorption bands in UV-Vis region due to oxygen – metal charge transfer [21]. The position of this electron transfer depends on the ligand field symmetry surrounding the metal (Me) site. For oxygen ligands, the energy transition between 220 and 260 nm is expected for tetrahedral Me compared while for octahedral – between 250 and 360 nm [21, 22]. As it was mentioned above the band at 330 nm is the strongest one which probably suggest the dominate presence of TiO_6 polyhedra. That is why in the IR spectra only one band at 470 cm^{-1} was observed and the band near 930 cm^{-1} corresponding to TiO_4 units is absent (Fig. 4).

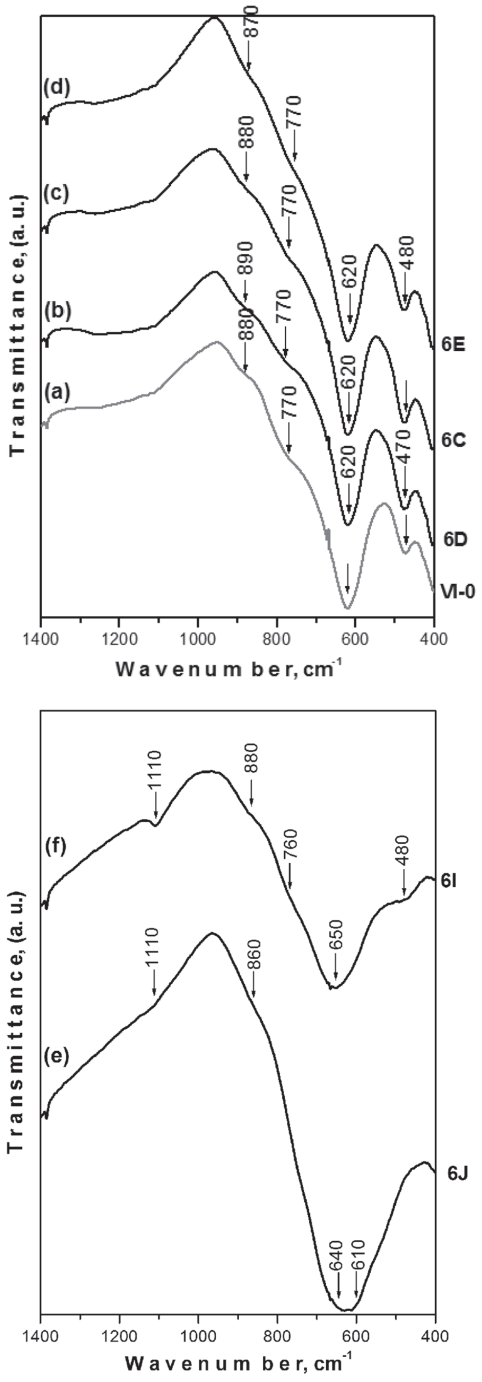

Fig. 4. IR spectra of investigated samples.

Dielectric measurements

The preliminary electrical measurements of as prepared sample 6E ($20TiO_2.50TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$) containing glass and several crystalline phases (Table 1) is with low conductivity and good dielectric properties (Fig. 6a, b). As it is seen there is no significant change of the dielectric losses with the temperature increasing up to 600 °C.

CONCLUSIONS

Applying the melt quenching method glasses were prepared in the multicomponent TiO_2 – TeO_2 – Bi_2O_3 – Nb_2O_5 – ZnO system and they exhibited

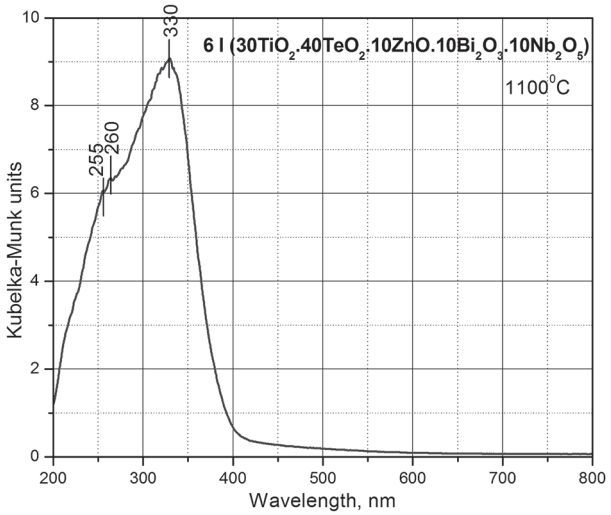

Fig. 5. UV-Vis spectrum of sample 6I ($30TiO_2.40TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$).

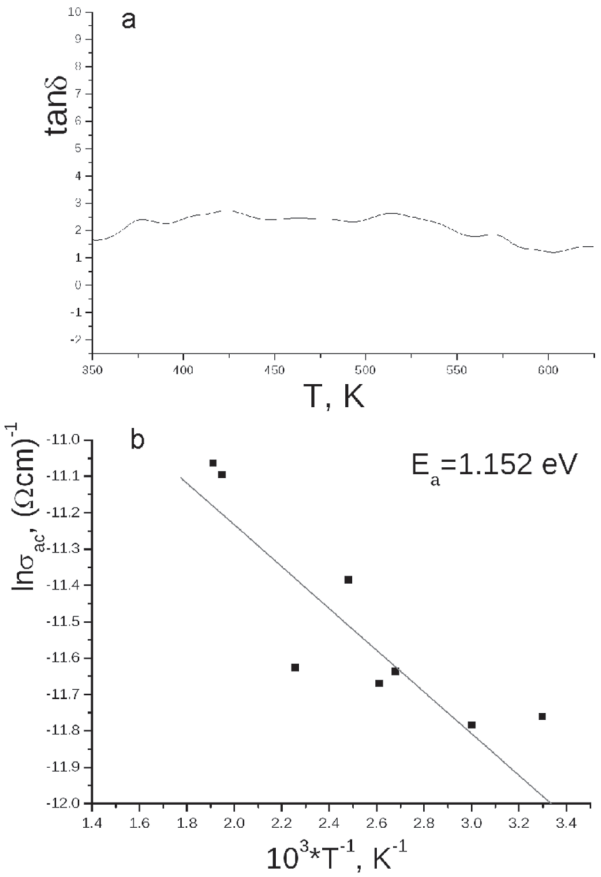

Fig. 6. Electrical measurements of sample 6E ($20TiO_2.50TeO_2.10ZnO.10Bi_2O_3.10Nb_2O_5$): (a) dielectric losses depending on temperature and (b) Arrhenius plot of activation energy.

good thermal stability up to 400 °C. By IR spectra is proved that the short range order of glasses is determined by TeO_4 structural units. It was established that the addition of above 20 mol% TiO_2 facilitated the crystallization tendency of investigated compositions. By free cooling of the melts, polycrystalline samples were obtained containing mainly $ZnTeO_3$, $TiTe_3O_8$ crystalline phases possessing good dielectric properties.

REFERENCES

1. V. K. Marghussian, Nano-Glass Ceramics, Elsevier Inc. (2015).
2. El-Malawany R, Tellurite glasses, Physical properties and data, CRC Press (2002).
3. Y. Wang, S. Dai, F. Chen, T. Xu & Q. Nie, *Mater. Chem. Phys.*, **113**, 407 (2009).
4. El Sayed Yousef, H. H. Hegazy, S. Almojadah, M. Reben, *Optics & Laser Technol.*, **74**, 138 (2015).
5. M. M. Ahmad, El Sayed Yousef, El Sayed Moustafa, *Physica B*, **371**, 74 (2006).
6. M. C. Wilding, G. Delaizir, Ch. Benmore, Y. Gueguen, M. Dolhen, J.-R. Duclere, S. Chenu, S. Sukenaga, P. F. McMillan, *J. Non-Cryst. Sol.*, (2016) (in press).
7. M. Udovic, P. Thomas, A. Mirgorodsky, O. Durand, M. Soulis, O. Masson, T. Merle – Mejean, J. C. Champarnaud – Mesjard, *J. Sol. State. Chem.*, **179**, 3252 (2006).
8. F. Chen, Q. Yu, B. Qiao, S. Dai, Q. Zhang, *J. Non – Cryst. Sol.*, **404**, 32 (2016).
9. M. Udovic, D. Suvorov, *J. Amer. Ceram. Soc.*, **90** (8), 2404 (2007).
10. K. Nakamoto, Infrared and Raman Spectra of Inorganic and coordination compounds, Wiley, New York, 1978.
11. P. Tarte, *Spectrochim. Acta*, **I8**, 467 (1962).
12. M. Arnaudov, V. Dimitrov, Y. Dimitriev, L. Markova, *Mater. Res. Bull.*, **17** (9) 1121 (1982).
13. Y. Dimitriev, V. Dimitrov, M. Arnaudov, *J. Mater. Sci.*, **18** (5), 1353 (1983)
14. M. Arnaudov, Y. Dimitriev, *Phys. Chem. Glasses*, **42** (2), 99 (2001).
15. R. Gegova, A. Bachvarova-Nedelcheva, R. Iordanova, Y. Dimitriev, *Bulg. Chem. Commun.*, **47** (1), 378 (2015).
16. K. Hanke, *Naturwissen*, **54**, 199 (4967).
17. H. Burger, W. Vogel, V. Kozhkharov & M. Marinov, J. Mater. Sci., **19**, 403 (1984).
18. K. Hanke, *Naturwissen*, **55**, 273 (1966).
19. G. Meunier and J. Galy, *Acta Cryst.*, **B27**, 602 (1971).
20. O. Yamaguchi, M. Morimi, H. Kawabata et al., *J. Amer. Ceram. Soc.*, **70**, c97 (1987).
21. R. S. Singh & S. P. Singh, *J. Mater. Sci.*, **36**, 1555 (2001).
22. R. J. H. Clarck, Chemistry of titanium and vanadium, Elsevier, Amsterdam, 1968.

ВЛИЯНИЕ НА TiO_2 ВЪРХУ ТЕРМИЧНАТА СТАБИЛНОСТ И КРИСТАЛИЗАЦИЯТА НА СТЪКЛА В СИСТЕМАТА TeO_2 – Bi_2O_3 – Nb_2O_5 – ZnO

Св. Ганев[1], С. Първанов[1], С. Славов[1], А. Бъчварова-Неделчева[2]*,
Р. Йорданова[2], Я. Димитриев[1]

[1] Химикотехнологичен и металургичен университет – София, бул. „Кл. Охридски“ 8, 1756 София, България
[2] Институт по обща и неорганична химия, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България

Постъпила октомври, 2016 г.; приета декември, 2016 г.

(Резюме)

В настоящото изследване като обект е избрана системата TeO_2–Bi_2O_3–Nb_2O_5–ZnO. Статията разглежда телуритни стъкла, съдържащи Nb_2O_5 и Bi_2O_3 до 10 мол.%, ZnO от 5 до 10 мол.%, докато съдържанието на TiO_2 варира от 5 до 50 мол.%. Получените стъкла са прозрачни и жълти на цвят (състави съдържащи над 20 мол.% TiO_2). Термичната стабилност на образците е определена чрез ДТА, използвайки разликата ΔT между екзотермичния пик на кристализация (T_x) и данните за температурата на застъкляване Tg (ΔT = 60–95 °C). Чрез рентгенофазов анализ са идентифицирани няколко кристални фази, сред които най-важни са $ZnTeO_3$ и $TiTe_3O_8$ (в състави, съдържащи над 20 мол.% TiO_2), притежаващи добри диелектрични свойства. Анализът на спектрите показа, че аморфната мрежа е изградена предимно от TeO_4 (TBP) структурни единици. Предварителните електрични измервания показаха незначителни изменения на диелектричните загуби с повишаване на температурата до 600 °C. Получените кристални образци са с ниска проводимост и добри диелектрични свойства.