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Thermochromic behavior of tellurite glasses

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ABSTRACT

Thermochromic behavior of tellurite glasses in the TeO_2–WO_3–A_2O (A_2O, A = Li, Na, K) system was investigated. Transmittance in visible region, absorption edge and optical band gap energy were determined at different temperatures below glass transition temperature. Reversibility of thermochromic behavior was tested using repeated heating and cooling measurements. The absorption edge values shifted towards longer wavelengths with increasing temperature and shift rate of absorption edge was found in the range of -3.94×10^{-4} and -8.86×10^{-4} eV/K similar to those of conventional semiconductor materials. Band gap energy values were found to decrease with increasing temperature lying in the range 1.81–2.83 eV. Tellurite glasses showed reversible thermochromic behavior and expected to find use in thermochromic applications. Good semiconducting property of tellurite glasses is found to be the cause of thermochromism.

1. Introduction

Chromic glasses have recently attracted great attention both scientifically and industrially as a result of an interest on discovering new glass systems which give automatic responses to changes in environmental conditions. Studies on chromic glasses have been mainly focused on electrochromic, photochromic and thermochromic glasses which have ability to change their optical properties reversibly with the change in electrical current, light and temperature, respectively. Most of the developments on chromic systems have been realized with electrochromic and photochromic glasses, whereas there exist limited number of works on thermochromic glasses. Although studies on thermochromic glasses are mostly concentrated on thin-film coated glasses for energy efficient window applications (especially VO_2-based coatings), there still has been a search for bulk glasses showing thermochromism. In this regard, until today few studies on thermochromic bulk glasses have been realized [1–7].

To the best of our knowledge, first study on thermochromic bulk glasses was realized by Abe et al. on phosphate glasses in the K_2O–B_2O_3–Al_2O_3–P_2O_5 and K_2O–Al_2O_3–P_2O_5 systems. Later Kawashima et al. also studied thermochromic behavior of phosphate glasses in CaO–P_2O_5, CaO–Al_2O_3–P_2O_5 and K_2O–B_2O_3–Al_2O_3–P_2O_5 systems. Both studies reported that the coloring in phosphate glasses is due to the change in the molecular state of colloidal phosphorus formed in the glass [1,2]. In their works on different bismuthate glasses, Sen et al. and Chen et al. found out that the thermochromic property in bismuthate glasses results from the temperature dependence of the expansion of the lattice and mainly due to the electron–phonon interactions [3–5]. Li et al. investigated temperature and compositional dependence of optical absorption edge in glasses containing high amount of PbO and TeO_2 (80 wt.%) and concluded that the shift of absorption edge in these glasses can be attributed to the polarizability of O–Pb and O–Te bonds [6]. In their study on thermochromic property of tellurite glasses containing transition metal oxides, Inoue et al. reported that transition metal oxides are compound semiconductors and they change their optical properties due to semiconductor to metal phase transition. Therefore, they concluded that tellurite glasses containing transition metal oxides show thermochromic property due to their high thermal expansion rate [7].

Tellurite glasses have drawn much attention as promising candidates for many opto-electronic applications due to their advantageous properties, such as high refractive index, relatively low-phonon energy, good visible and infrared transmissivity, suitability for doping with rare earth elements in a wide range and good electrical properties owing to the unshared pair of electrons of the TeO_4 groups that do not take part in bonding. It is known that TeO_2 does not form glass under normal quenching conditions without addition of a secondary component. Therefore, addition of secondary components are required to synthesize tellurite glasses.

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Table 1
Values of glass transition (T_g) and first crystallization (T_{c1}/T_{p1}) temperatures and glass stability (ΔT) of TeO_2–WO_3–A_2O (A = Li, Na, K) glasses.

Sample ID	TeO_2 (mol%)	WO_3 (mol%)	Li_2O (mol%)	Na_2O (mol%)	K_2O (mol%)	T_g (°C)	T_{c1}/T_{p1} (°C)	ΔT (°C)
T80W20	80	20	–	–	–	349	447/492	98
T80L20	80	–	20	–	–	268	307/319	39
T80N20	80	–	–	20	–	250	352/366	102
T80K20	80	–	–	–	20	234	303/321	69
T80W10L10	80	10	10	–	–	305	380/390	75
T80W10N10	80	10	–	10	–	308	342/369	34
T80W10K10	80	10	–	–	10	309	403/428	94
T50W25L25	50	25	25	–	–	323	505/*	182
T50W25N25	50	25	–	25	–	309	360/373	51
T50W25K25	50	25	–	–	25	284	340/362	56

*: undetermined value.

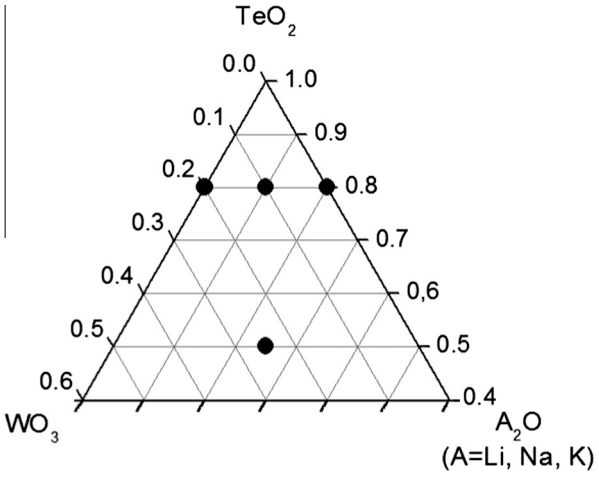

Fig. 1. Compositions of the prepared glasses.

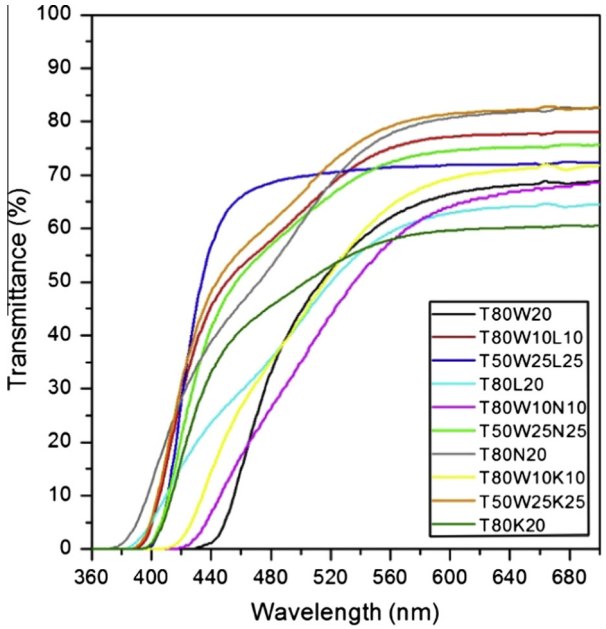

Fig. 2. Transmittance spectra of TeO_2–WO_3–A_2O (A = Li, Na, K) glasses at room temperature.

Nature, concentration and field strength of the modifier oxides in multi-component tellurite systems substantially determine the optical and electrical properties of glasses [8]. In this regard, combination of TeO_2 with two or more components yields stable glasses and provides control of the desired properties [9,10]. Addition of WO_3 to tellurite glass network enhances chemical stability and devitrification resistance, gives possibility to modify the composition by a third, fourth, and even fifth component and makes the electronic transitions possible in the glass network [11–14]. As a transition metal oxide, tungsten oxide has two different valence states, namely W^{5+} and W^{6+}. The hopping of electrons between these two valence states is responsible for the conduction in WO_3 containing glasses [15]. Addition of alkali oxides (A_2O, A = Li, Na, K) to the tellurite glass network improves thermal stability, generates non-bridging oxygen sites and makes ion transport suitable [8,9,16,17]. In the present work due to these favorable properties we incorporated WO_3 and alkali oxides (A_2O, A = Li, Na, K) to obtain tellurite glasses.

Table 2
Values of absorption edge at 25 °C and 240 °C and shift rate of absorption edge for TeO_2–WO_3–A_2O (A = Li, Na, K) glasses.

Sample ID	Absorption edge at 25 °C (nm)	Absorption edge at 240 °C (nm)	Shift rate of absorption edge (10^{-4} eV/K)
T80W20	428	441	−3.94
T80L20	382	401	−6.85
T80N20	369	379	−4.13
T80K20	392	406	−5.07
T80W10L10	389	410	−3.94
T80W10N10	418	437	−5.95
T80W10K10	385	401	−5.92
T50W25L25	395	418	−8.29
T50W25N25	393	406	−4.47
T50W25K25	392	407	−8.86

In order to develop new glasses for thermochromic applications, the knowledge of optical features of these glasses depending on temperature is crucial. In this paper, to the best of our knowledge, we report for the first time a detailed study on the investigation of thermochromic behavior in tellurite glasses. In this regard, temperature dependent spectroscopic analysis were realized and transmittance in visible region, absorption edge, shift rate of absorption edge and optical band gap energy values and reversibility of thermochromic behavior were determined.

2. Experimental procedures

To investigate thermochromism in tellurite glasses, different ternary glass compositions in the TeO_2–WO_3–A_2O (A_2O, A = Li, Na, K) system were prepared together with selected samples from their binary systems (TeO_2–WO_3, TeO_2–Li_2O, TeO_2–Na_2O, TeO_2–K_2O) using a conventional melt-quenching technique. In order to synthesize glass samples, high purity chemicals of TeO_2 (99.99% purity, Alfa Aesar Company), WO_3 (99.8% purity, Alfa Aesar Company), Li_2CO_3 (99.5% purity, Alfa Aesar Company), Na_2CO_3 (99.0% purity, Alfa Aesar Company) and K_2CO_3 (99% purity, Alfa Aesar Company) were used as starting materials. After weighing and thoroughly mixing, batches of 7 g in weight were melted in a platinum crucible