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Review

Tungsten-based glasses for photochromic, electrochromic, gas sensors, and related applications: A review

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ABSTRACT

The present work focuses on reviewing the scientific literature on various types of tungsten-based glasses such as tungsten–phosphate, tungsten–tellurite, tungsten–borate glasses, tungsten–germinate, tungsten–antimonate, and non-traditional tungsten oxide-containing glasses. The glass formation, structure, thermal, some chemical, physical and characterization of materials are discussed. Tungsten-based glasses show a remarkable potential for many photochromic, electrochromic and gas sensing applications.

1. Introduction

Tungsten trioxide and more complex tungsten oxygen compounds are very promising inorganic materials which exhibit excellent electrochromic, photochromic and gasochromic properties and it has been widely investigated to be used in electrochromic, gasochromic, solar energy, optical modulation, writing–reading–erasing optical devices, flat panel displays, gas, humidity and temperature sensors. Lots of the unique properties characteristic of tungstates can be realized in an amorphous state of the materials. R_2O–WO_3 glasses (R = Li, Na, K) exhibit high ionic conductivity and electrochrmic properties. Borate glasses containing tungsten ions are electronically conducting semiconductors (coexistence of W^{5+} and W^{6+} ions). Glass-ceramics (dielectric) segnetoelectric materials are obtained in the system $(1 - x)Li_2B_4O_7 - xBi_2WO_6$ ($0 \le x \le 0.35$) comprising nanocrystals of Bi_2WO_3. Complex tungsten–tellurite glass systems doping with a high concentration of rare-earth elements: TeO_2–WO_3–Ln_2O_3 (Ln = La, Er) are now considered to be one of the most perspective materials for the development of high-performance laser sources, amplifiers and fiber optics. The role of the WO_3 in the glasses is complicated, because of its high crystallization ability. WO_3 is a conditional glass former that is not able to form glasses itself with standard methods of vitrification. Its glass formation ability is significantly enhanced by the addition of other compounds. There are few data in the literature about the preparation of stable glasses having high WO_3 content, where WO_3 can be regarded as glass-forming oxide. The glass formation regions between 23 and 70 mol% WO_3 in binary R_2O–WO_3; R = Li, K, Na, Rb, Cs systems, have been determined applying rapid quenching techniques. The high critical cooling rates (5×10^5–10^6 K/s) have been applied for the amorphisation of compositions in WO_3–Nd_2O_3, WO_3–M_xO_y (M = Al, Sm, Eu, Gd, Dy, Ho) and BaO–Nd_2O_3–WO_3 systems, where the concentration of the M_xO_y oxides are in the range between 15 and 25 mol%. The existence of a large glass-forming domain (8–50 mol% of WO_3), whose extension strongly depends on quenching technique, has been found in TeO_2–WO_3 system. Glasses with high WO_3 content within a narrow concentration range (60–75 mol%) are obtained in tungstate systems containing simultaneously and other non-traditional glass formers such as V_2O_5, MoO_3, Bi_2O_3. WO_3 easier form glasses over a wide range of compositions in binary and more complex systems containing conventional glass forming oxides like P_2O_5, B_2O_3 and GeO_2. Stable binary P_2O_5–WO_3 glasses are obtained over a wide concentration range – up to 80 mol% WO_3. However, up to now there is not enough data for the glass formation in many component tungstate glass systems where WO_3 is a main glass former. On the other hand the literature review has

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shown that the structure of WO_3-based glasses and especially the coordination state of tungsten atoms is not well understood. The first structural studies have shown that amorphous WO_3 thin films are built up by strongly distorted, but well defined octahedra joined by vertices. The possibility to construct amorphous network containing only WO_6 octahedra has been also demonstrated by modeling. Participation of both WO_6 and WO_4 polyhedra in the structure of binary glasses in the R_2O–WO_3, R = Li, K, Na, Rb, Cs systems has been proven by IR spectroscopy. Some authors agree that tungsten oxide units in many component glasses are present in the network as WO_6 octahedra together with WO_4 tetrahedra. Other authors using different complimentary techniques suggested that only six-fold coordinated (WO_6) tungsten atoms exist in the glasses and they are enough for the formation of the amorphous network.

Having in mind the mentioned above, it can be concluded that WO_3 is an appropriate compound for the solving of general fundamental structural problems concerning the amorphous state and as well as for the preparation of new type of oxide glasses for technology.

The present review is devoted to the investigation of the state-of-the-art of glass formation tendency, structure and crystallization behavior of glasses in complex oxide systems containing high WO_3 content.

2. Tungsten–phosphate glasses

Among the classical glass forming oxides, P_2O_5 allows the preparation of stable glasses in combination with WO_3 over a wide concentration range up to 80 mol% of WO_3 [1]. Spectroscopic and other investigations have been used to characterize these glasses and it has been found that W atoms are present in octahedral coordination [2]. The glass structure consists of corner sharing WO_6 octahedra and PO_4 tetrahedra in the binary tungstophosphate glasses. Glasses containing 80% of WO_3 are very prone to crystallization indicating that glasses containing only corner sharing octahedra may not be stable. Some of these glasses, particularly those rich in the hexavalent oxides are coloured (blue, green and often brown). These colors arise due to the presence of reduced forms of the tungsten ions (W^{5+}) and their d–d transitions are responsible for their color [2]. Stable glasses have been obtained in the system $SbPO_4$–WO_3 [3]. These glasses present good thermal stability and high refraction index. Structural results suggest the presence of two distinct glass networks. One consisting of random phosphate chains with WO_6 octahedra inserted along the structure. The second one is formed by linking together the WO_6 octahedra as the tungsten oxide concentration increases. Glasses are photosensitive when exposed to visible lasers and the photochromic effect can be erased by heat treatment. XANES data suggests the presence of W^{5+} species in the exposed glass [3]. The local order around tungsten atoms in various sodium tungstophosphate glasses has been investigated using extended X-ray absorption fine structure (EXAFS). The obtained results show that tungsten atoms are present in six-coordinated environment in these glasses [1,2]. Araujo et al. [4] have reported the results of a systematic structural study of the binary $NaPO_3$–WO_3 system as a function of composition. In particular single and double resonance high-resolution solid state NMR techniques (including two-dimensional resolved spectroscopy) as well as Raman spectroscopy have been used to develop a fundamental understanding of the structural network evolution of these $NaPO_3$–WO_3 glasses. Addition of WO_3 to the $NaPO_3$ glass melt leads to a pronounced increase in the glass transition temperatures, suggesting a significant increase in network connectivity. At the same time Raman spectra indicate that up to about 30 mol% WO_3 the tungsten atoms are linked to some non-bridging oxygen atoms ($W–O^-$ or W═O bonded species), suggesting that the network modifier sodium oxide is shared to some extent between both network formers. W–O–W bond formation occurs only at WO_3 contents exceeding 30 mol %. More recently mixed alkali tungstate phosphate Li_2O–Na_2O–WO_3–P_2O_5 glasses have been synthesized and their thermal and electrical, properties have been investigated [5]. It was found that dc conductivity and the glass transition temperature present minima when mixing Li_2O and Na_2O. It was also shown that the isothermal variation of the electrical conductivity is sensitive to the temperature; the higher the temperature is, the lower the magnitude of the minimum is observed. Defect generation accompanying site rearrangement when Na_2O replaces Li_2O results in the shift of T_g to lower temperatures [5]. Studies concerning the synthesis, structure, elastic properties and crystallization behavior of glasses in the M_2O–MgO–WO_3–P_2O_5 (M = K, Rb, Cs) system have been also reported in the literature [6,7]. Raman and IR studies have shown that these glasses have very similar structure. The main building blocks are pyrophosphate groups, WO_6 octahedra and magnesium–oxygen polyhedra. The dc conduction in these glasses is controlled by hopping of small polar ions. The potassium containing glass was shown to be very stable whereas the rubidium and cesium glasses have significantly higher tendency for crystallization and phase separation. The observed differences in the crystallization behavior of the studied glasses can be most likely attributed to differences in viscosity of the melts and stability of different crystalline phases due to significant differences in ionic size of alkali metal ions. Alkali niobium tungstate phosphate glasses –A_2O–WO_3–10Nb_2O_5–P_2O_5, A = Li, Na, K have been also synthesized and they were studied by Raman, X-ray, SEM and DTA analysis [8,9]. It was found that the introduction of tungsten into these alkali niobiophosphate glasses induces the creation of additional non-bridging oxygen ions and/or the formation of larger niobium- and/or tungsten-containing structural units such as WO_6/NbO_6 octahedra in the glass network. PbO–WO_3–P_2O_5 glasses have been extensively studied in recent years [10–12]. These glasses present good thermal stability as well as high transition temperature values associated with structural changes induced by WO_3 incorporation. Successive incorporation of WO_3 into $AgPO_3$ glass (up to 50 mol%) results in a dramatic increase of the glass transition temperature with a T_g maximum near x = 0.5 [13]. FTIR, Raman and NMR data indicate the formation of P–O–W connectivities which initially crosslink between the different metaphosphate chains, while XANES data obtained at the W-L1 absorption edge suggest that tungsten is mainly octahedrally coordinated. A broad glass forming region was observed in the system (100-x)[0·5ZnO.0·1B_2O_3.0·4P_2O_5].$x$$WO_3$ for x = 0–50 mol% WO_3, but glasses with 45–50 mol% WO_3 contain microinclusions of β-WO_3 crystallites which are not detected by X-ray diffraction [14]. The chemical durability and thermal stability of the glasses is very good. The highest thermal stability, evaluated as the difference between crystallization temperature and glass transition temperature, is for glasses containing 10–15 mol% WO_3. According to the studies of Raman spectra, tungsten oxide incorporates into the structural network most probably in the form of WO_6 octahedra. These octahedra form clusters via W–O–W bonds, the number of which increases with increasing WO_3 content. The incorporation of WO_6 octahedra into the structural network is associated with the depolymerisation of phosphate chains. The NMR spectra revealed the formation of diphosphate and orthophosphate groups and P–O–W and also B–O–W bonds, as well [15]. Blue luminescent WO_3–P_2O_5–ZnO glasses were fabricated, and the XRD, Raman spectra and luminescence properties of the WO_3–P_2O_5–ZnO ternary glass system were investigated [15]. XRD measurements proved the amorphous phase of the glasses. Using Raman spectroscopy, the existence of WO_6 groups in the glass was verified. The results of the luminescence spectra and the decay curve were compared with the luminescence in $ZnWO_4$ crystals. Due to the similarities found between the glass and the crystal, it was concluded that the origin of the luminescence for glasses made under both melting conditions is the same as that of $ZnWO_4$ crystals. Hence, the band at 320 nm was assigned to an electronic excitation from the O (2p) to the W (5d) levels, leading to the decay of the WO_6 groups at 530 nm.

During the last few years, tungstate fluorophosphate glasses have been intensively studied in terms of their structure, crystallization behavior and optical properties [16–22]. Tungsten oxide increases the