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Synthesis, characterization and optical properties of non-traditional tellurite–selenite glasses

A. Bachvarova-Nedelcheva [a,*], R. Iordanova [a], K.L. Kostov [a], V. Ganev [b], St. Yordanov [c]

[a] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[b] Institute of Mineralogy and Crystallography "Acad. I. Kostov", Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[c] Central Laboratory of Solar Energy and New Energy Source, 72, Tsarigradsko Shose Blvd., 1784 Sofia, Bulgaria

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ABSTRACT

This study continues our investigations on non-traditional tellurite–selenite amorphous materials. Two glasses containing TeO_2, SeO_2, MoO_3 and V_2O_5 were obtained at high oxygen pressure (P = 36 MPa) using pure oxides as precursors. The real bulk chemical composition of both glasses was verified by LA-ICP-MS method. The glasses were characterized by X-ray diffraction, Scanning Electron Microscopy (SEM), Differential Thermal Analysis (DTA), UV–Vis, XPS, IR and EPR spectroscopy. According to DTA the glass transition temperature (T_g) is below 300 °C. Both glasses were subjected to heat treatment (300 °C – 12 h) and as a result no crystallization was observed. The main building units (TeO_3, TeO_4, Mo_2O_8, and SeO_3) were determined by IR and X-ray photoelectron spectroscopy and the existence of mixed bridging bonds only, which build up the amorphous network. It was established by UV–Vis that the obtained glasses are transparent above 550 nm and they were red colored.

1. Introduction

The synthesis and characterization of tellurite glasses was widely studied in the Department of Silicate technology in UCTM – Sofia and in the 1980–1990s years of the XX century this topic was a traditional subject for the Department [1–3]. A lot of data for tellurite glasses was collected in the Mallawany's monography [4]. Although TeO_2 cannot be vitrified alone by traditional methods, high transparent tellurite glasses could be obtained simply by introducing other metal oxides (e.g. transition metal oxides, alkaline oxides and alkaline-earth oxides) without the addition of any conventional glass former, which was first reported by Rawson and Stanworth [5,6]. The tellurite glasses continue to provoke interest due to their high refractive indices, low melting temperatures and high dielectric constants as well as their good infrared transmissions. It is well known that they are considered as promising materials for non-linear optical devices [4,7–11], optical fiber amplifiers [12], electronic switching effects [13], etc. Quite recently, metal oxides such as Bi_2O_3, Sb_2O_3, MoO_3 and Nb_2O_5 have been added to the tellurite glass system in order to enhance their optical behavior [14–16]. Obviously, the investigations on the structure and properties of different multicomponent tellurite glasses are still not exhausted. On the other hand, selenite glasses are a new exotic class of non-traditional glasses that have not been enough studied up to now. As it is well known the main difficulty in the synthesis of this type of glasses is the rapid volatilization of selenite melts and the sublimation of SeO_2 at atmospheric pressure and temperatures above 315 °C. It was already established that in different two-, three and multicomponent selenite systems it is possible to obtain a selenite glass even at a low cooling rate, particularly if the second components are also glass-forming oxides [17,18]. In our previous investigations different colored selenite glasses with specific optical properties were obtained [19]. Some complicated compositions should be potential candidates for technological applications as amorphous semiconductors and superionic materials, infrared transmission components, in non-linear optical devices, sensors, reflecting windows, soluble microfertilizers, etc. [20–27]. The main advantage of the introduction of SeO_2 is its ability to decrease the melting temperature of glass compositions and to modify their optical properties [28–31].

Recently, our team obtained an orange colored glass containing TeO_2, SeO_2, MoO_3 and La_2O_3 and its thermal stability, local order as well as optical properties were investigated [33]. Moreover, the actual chemical composition of the glass was determined by different analytical methods in order to verify the content of SeO_2 and TeO_2.

* Corresponding author. Tel.: +359 (2) 979 63 17; fax: +359 (2) 870 50 24.
E-mail address: albenadb@svr.igic.bas.bg (A. Bachvarova-Nedelcheva).

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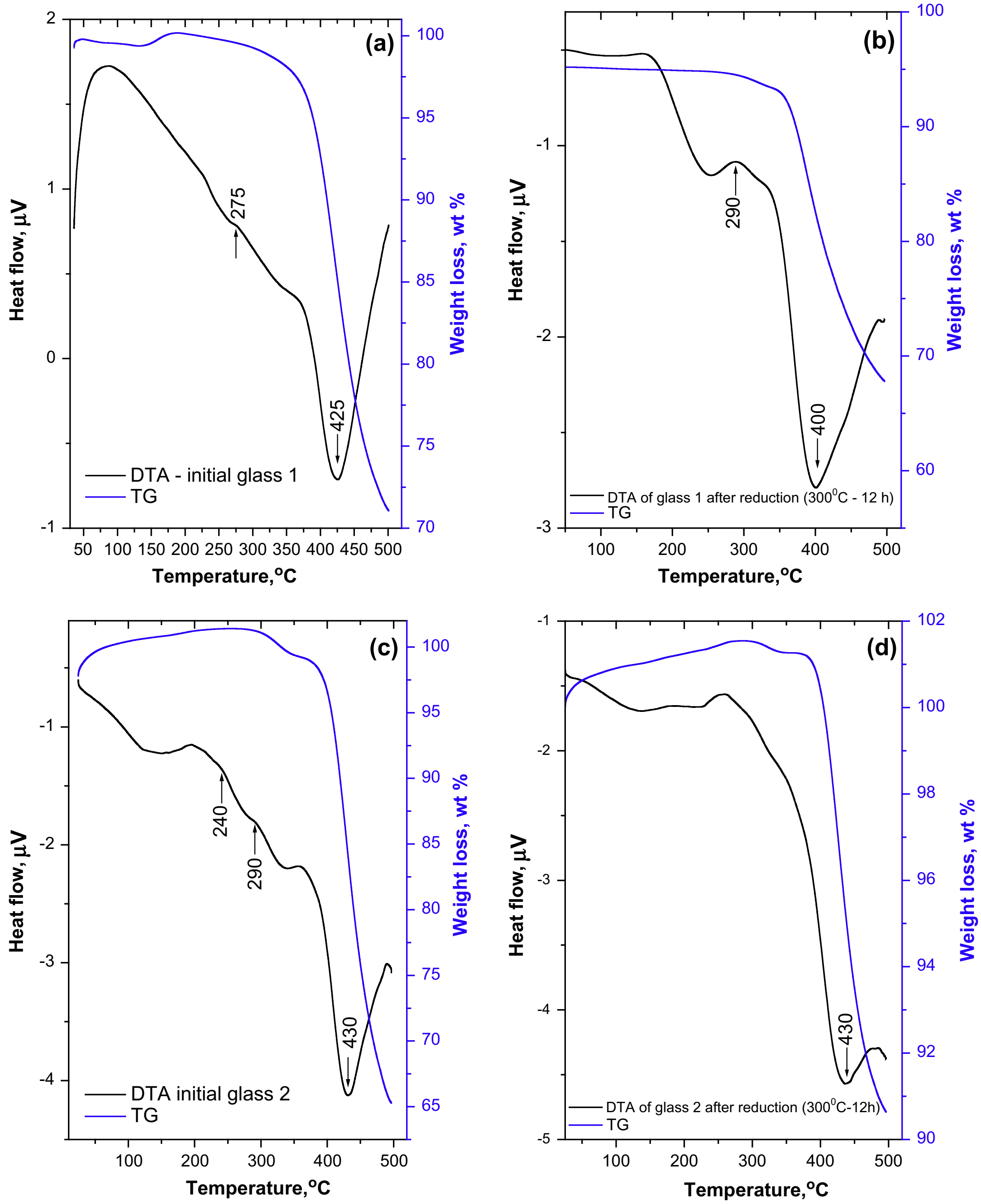

Fig. 1. DTA curves of the investigated glasses: a, b – glass 1 and c, d – glass 2, before and after heat treatment.

Despite, the fact that the glass synthesis was performed in an autoclave at oxygen pressure $P = 35–36$ MPa it was found a difference in the composition before and after melting. The presence of elementary Te^0 and Se^0 as well as Mo^{5+}, probably are responsible for the darkening of the glass after heat treatment in a reduction atmosphere. Bearing in mind our experience in obtaining non-traditional glasses [32–34] as well as latest results in this topic [35–41], the present study is a continuation in this direction, where SeO_2, TeO_2 and MoO_3 are the main oxide components and V_2O_5 was added as a coloring agent. The purpose of this study is to establish the thermal stability of the glasses in oxidizing and reduction atmosphere, their optical properties and main structural units building up the amorphous network.

2. Experimental

2.1. Glass preparation

The investigated compositions were selected on the basis of our previous results on the glass formation in various model selenite systems [18,31,32]. The problem with these glasses is their high volatility and the sublimation of SeO_2 at atmospheric pressure. The glass samples were prepared using reagent grade SeO_2 (Reachim, chem. pure), TeO_2 (Merck, p.a.), MoO_3 (Merck, p.a.), V_2O_5 (Merck, p.a.) and Nb_2O_5 (Alfa-Aesar, p.a.) as starting compounds. The weighing and homogenizing of the batches was carried out in a dry box. In order to avoid SeO_2 sublimation, the melting was