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# New phospho-tellurite glasses with optimization of transition temperature and refractive index for hybrid microstructured optical fibers

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ABSTRACT

The glass formation and compositional dependences of glass thermal properties and optical properties were investigated in $TeO_2$–ZnO–$Na_2O$–$P_2O_5$ system. The refractive index at 1.55 μm and glass transition temperature varied in a wide range from 1.513 to 2.036 and from 265 °C to 376 °C by controlling of the $TeO_2/P_2O_5$ and ZnO/$Na_2O$ content, respectively. These properties enable phospho-tellurite glasses with large freedom in designing and fabrication of hybrid microstructured optical fiber. The structures of glasses were investigated by Raman spectra to understand their dependence of structure on composition. Using the present glasses, some hybrid microstructured optical fibers with various dispersion profiles were designed.



## 1. Introduction

Photonic crystal fibers (PCFs) and microstructured optical fibers (MOFs) have attracted much interest in the past decade, due to their special guiding properties [1,2]. One of the most appealing features of PCFs and MOFs is their high flexibility in the controlling of chromatic dispersion. In silica PCFs, the chromatic dispersion can be tailored effectively by manipulating the geometrical parameters of multi-rings air holes [3–5]. Due to the large material dispersions and the low softening points of non-silica glasses, the controlling of chromatic dispersion is much more difficult than that in silica PCFs and MOFs. To resolve this problem, one of the promising way is using different glasses as core and cladding glass to make the hybrid fiber, whose dispersion can be well tailored by the refractive index distribution i.e., structural size of each segment and refractive index contrast [6]. From a viewpoint of fabrication, solid core and cladding are more controllable than air holes. Recently, some hybrid microstructured optical fibers (HMOFs) with tailored dispersion have been demonstrated [6–8]. In such case the composition and properties of glass are very important.

$TeO_2$ and $P_2O_5$ are well known classic glass network formers. Based on them, many tellurite glass and phosphate glass systems have been investigated and developed for various applications such as laser media, optical amplifier, nonlinear optical devices and biomedical materials [9,10]. Tellurite glasses are favorable media for highly nonlinear fibers due to the high nonlinear refractive index and wide transmission window. The refractive index of typical tellurite glass is ~2.0 at 1.55 μm, which is really high compared to that of phosphate glass. By adjusting contents of glass network modifiers the refractive index can be tailored in the scale of ~0.1 [9], however, this value is really smaller compared with the requirement of refractive index contrast for chromatic dispersion tailoring. Besides glass network modifiers, introducing glass network formers can adjust the refractive index, even in a larger scale. Tellurite glasses with a second glass network former have been reported in $TeO_2$–$P_2O_5$, $TeO_2$–$GeO_2$ and $TeO_2$–$B_2O_3$ systems [11–14]. Based on $TeO_2$–$P_2O_5$ system various glasses were designed and the glass-forming regions, glass structures and properties were also investigated in past decades [13,14]. In this paper, we report the glass formation, structure compositional dependence of thermal properties and optical properties in the $TeO_2$–ZnO–$Na_2O$–$P_2O_5$ system with the aim of realizing tellurite hybrid optical fibers with tailored chromatic dispersions.

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## 2. Experiment and characterization

In order to define the glass formation region in the $TeO_2$–ZnO–$Na_2O$–$P_2O_5$ system, glasses with the composition denoted in the quaternary diagram shown in Fig. 1 were prepared by the conventional melt quenching method. About 10 gm batches were prepared for each composition from reagent grade $TeO_2$, ZnO, $Na_2CO_3$ and $P_2O_5$ and well mixed in a dry-nitrogen-purged glove box. The batches were then melted in an electrical furnace, under an $O_2$ atmosphere, in a covered platinum crucible. It is known that reduction of $Te^{4+}$ coloration occurs in melting phospho-tellurite glasses. This coloration degrades the transparency of optical glasses. Oxygen flow can restrain the reduction of $Te^{4+}$ in some scale during the melting process. But the coloration will become much serious and make the glass dark in appearance when the melting temperature is higher than 1000 °C. In this experiment, the melting temperature was set at 850 °C for each composition in the beginning, and then increased to 1000 °C for the unmelted glasses. All the glasses were melted for 15 min and then the glass melt was poured onto a stainless steel plate preheated to 300 °C. Each glass sample was annealed at 300 °C for 5 h to release the thermal stress associated with these glasses during the quenching process. Finally the transparent samples were cut to a size of around 15 mm × 15 mm × 5 mm and then optically polished.

Refractive indices were measured by the prism coupling method (Metricon Model 2010) at four wavelengths viz. 632.8, 974, 1320, and 1544 nm, with accuracy better than ±0.001. The Raman spectra were measured with a JASCO NRS 2100 spectrometer in the spectral range 20–1700 $cm^{-1}$. The glass sample was excited with a solid state laser at 532 nm with a power of ~100 mW. The spectrum was observed in the quasi-back scattered mode. Raman measurements were performed in the VV polarization geometry for the exciting and back scattered light. The digital intensity data were recorded at intervals of 1 $cm^{-1}$.

The thermal properties were measured by a differential scanning calorimeter (Rigaku, ThermoPlus DSC 8270). A small piece of bulk glass was ground down to powder with diameters of less than 120 μm before the DSC measurement. About 30 mg powder was heated in a platinum pan at a rate of 10 K/min, in the temperature range of 25–600 °C. The glass transition temperature ($T_g$) was determined from the tangent intersection of endothermic peaks in the DSC curve and onset crystallization temperature ($T_x$) was obtained from the tangent intersection of exothermic peak. The softening temperature ($T_s$) of the glasses was measured using a thermo-mechanical analyzer (TMA) (Rigaku ThermoPlus TMA 8310). After optical measurements, glass samples were cut into 15 mm × 5 mm × 5 mm and measured with a reference of standard silica glass rod. A load of 10 g was applied on the sample during the measurement.

## 3. Results and discussion

### 3.1. Glass formation in the $TeO_2$–ZnO–$Na_2O$–$P_2O_5$ system

Fig. 1 shows the phase diagram for the $TeO_2$–ZnO–$Na_2O$–$P_2O_5$ system, depicting the various compositions investigated in this work. To make it clear, sections based on the ZnO content were taken from the quaternary diagram and shown as $TeO_2$–$Na_2O$–$P_2O_5$ ternary diagrams Z0, Z10, Z20, Z30 and Z40 with ZnO of 0, 10, 20, 30 and 40 mol%, respectively. Composition with high ZnO content (ZnO > 40 mol%) maybe form glass but not included in the present study, because the high ZnO content raises melting temperature and tends to induce coloration. As shown in Fig. 1, undissolved samples which are indicated by red diamond, appear in high ZnO and $P_2O_5$ region. In Z0 and Z10 all the compositions can be melt well at temperatures below 1000 °C. With increasing the ZnO content to 20 mol%, the melting temperature of glass was raised. And samples that contain high $P_2O_5$ content ($P_2O_5 \geqslant 60$ mol%) became infusible at 1000 °C. While increasing the ZnO content to 40 mol%, the unmelted compositions appeared in the high $P_2O_5$ region and also the high $Na_2O$ region. Furthermore, the glass-forming region became narrow with increasing the ZnO content, because glass intermediate oxide ZnO cannot form glass network. With the high ZnO contents, the crystallization tendency is enhanced and glass formation ability is decreased. In the present glass system, $TeO_2$ and $P_2O_5$ are glass network formers while ZnO and $Na_2O$ act as glass intermediate oxide and network modifier.

For systems containing two glass network formers simultaneously, there is a tendency of showing dominance by each glass network formers to form the main structure network. As their

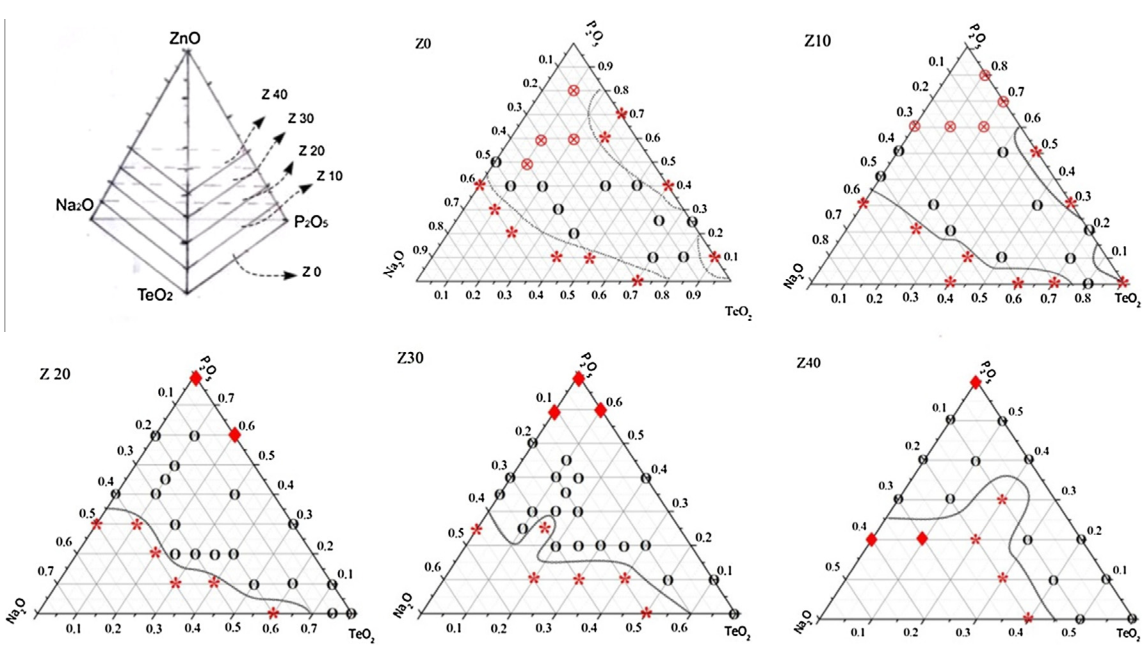


**Fig. 1.** Glass-forming region of $TeO_2$–ZnO–$Na_2O$–$P_2O_5$ system: O – transparent glass; ⊗ – transparent and deliquescent; ✱ – devitrified; ♦ – unmelted.