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Effect of alkali metal oxides R_2O (R = Li, Na, K, Rb and Cs) and network intermediate MO (M = Zn, Mg, Ba and Pb) in tellurite glasses

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ABSTRACT

A systematic characterization of optical, chemical and thermo-mechanical properties of R_2O–MO–TeO_2 glasses as function of alkali metals as network modifiers and network intermediate was performed. Properties such as thermal expansion coefficient (α), glass transition temperature (T_g), refractive index (n), transmittance, chemical durability (DR), density (ρ) and the third-order nonlinear optical susceptibility ($\chi^{(3)}$) were measured and it was found that both components R_2O and MO, have great influence on such properties. Experimental results indicate that alkali metals with small ionic radii improve chemical durability (DR) and mechanical (α, T_g) properties. They also increase n and $\chi^{(3)}$. Lower thermal expansion coefficient was obtained for Zn and Mg while better chemical durability corresponds to Pb and Zn.

1. Introduction

The development of new materials which combine desirable thermo-mechanical properties with good laser and optical quality is necessary for a high performance laser and optical amplifiers. Glasses that were composed of only glass former do not have the ability to provide all these properties. Thus, the incorporation of network modifiers is necessary to achieve these requirements. Recently, a lot of work on glass composition has been reported in silica, silicate, borate and phosphate glasses. There, the effect of alkali metals and alkali earth has been studied in order to improve the thermo-mechanical properties as well as optical and physical properties [1–13]. Silica glasses are one of the most studied materials for laser and amplification applications. However, concentration quenching appears when glasses are doped at high concentration reducing the performance of amplifiers and lasers [14,15]. In addition, their limited bandwidth also limits the transmission capacity. In contrast, silicate and phosphate glasses can be doped at higher concentration than silica, and high gain has been reported [16,17]. However, no high Er^{3+} doped phosphate or silicate glasses combined with a broad bandwidth have been reported. Tellurite glasses resolve those drawbacks providing high rare earth solubility and broad bandwidth over 80 nm. With such properties, they have received great attention due to their potential use in EDFAs [18,19]. In addition, tellurite glasses exhibit other properties such as wide transmission range, high linear and nonlinear refractive index, good chemical durability, high density, good glass stability and low glass transition temperature. These glasses have been considered as a potential candidate for use in nonlinear optical devices because of their large third-order nonlinear optical susceptibility [20].

It is well known that the spectroscopic, physical and thermo-mechanical properties of glasses depend on the glass composition. For example, the binary system TeO_2–ZnO has good chemical durability but low rare earth solubility. The addition of Na_2O improves the rare earth solubility [21] and makes it suitable for the fabrication of optical waveguide devices by ion-exchanged process [22]. However, the sodium content should be appropriate because high alkali concentration usually presents poor chemical durability. Thus, it is important to know the chemical elements that should be added into the host in order to design glasses with desirable optical properties and high performance. The right selection of glass composition depends on the application and often is a compromise among many factors. In the present work, a systematic study of physical and chemical properties of TeO_2 glasses as a function of network modifiers is reported. Twenty tellurite glasses were prepared to explore and compare the effect of alkali metals and network intermediate on the thermo-mechanical, physical and optical properties. The glasses are divided into four batches R_2O–PbO–TeO_2, R_2O–ZnO–TeO_2, R_2O–BaO–TeO_2, and R_2O–MgO–TeO_2 to facilitate the analysis of the measured properties. The code and glass composition are shown in Table 1. This work emphasizes the importance of the glass composition used in the design of optical amplifiers, lasers and other applications to achieve the best properties.

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Table 1
Code and tellurite glass composition (mol%)

Code	Te	Pb	Zn	Ba	Mg	Cs	Rb	K	Na	Li
T11	70	20	–	–	–	10	–	–	–	–
T12	70	20	–	–	–	–	10	–	–	–
T13	70	20	–	–	–	–	–	10	–	–
T14	70	20	–	–	–	–	–	–	10	–
T15	70	20	–	–	–	–	–	–	–	10
T21	70	–	20	–	–	10	–	–	–	–
T22	70	–	20	–	–	–	10	–	–	–
T23	70	–	20	–	–	–	–	10	–	–
T24	70	–	20	–	–	–	–	–	10	–
T25	70	–	20	–	–	–	–	–	–	10
T31	70	–	–	20	–	10	–	–	–	–
T32	70	–	–	20	–	–	10	–	–	–
T33	70	–	–	20	–	–	–	10	–	–
T34	70	–	–	20	–	–	–	–	10	–
T35	70	–	–	20	–	–	–	–	–	10
T41	70	–	–	–	20	10	–	–	–	–
T42	70	–	–	–	20	–	10	–	–	–
T43	70	–	–	–	20	–	–	10	–	–
T44	70	–	–	–	20	–	–	–	10	–
T45	70	–	–	–	20	–	–	–	–	10

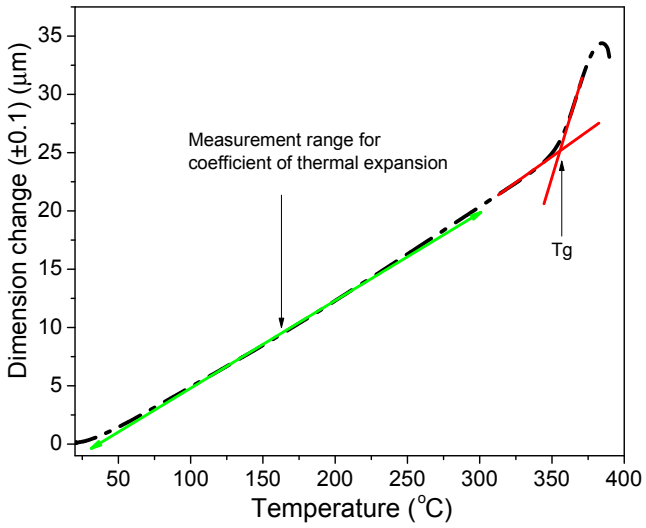

Fig. 1. Thermal expansion and glass transition temperature curve.

2. Experimental procedure

All samples were prepared from the starting chemical constituents tellurium oxide (TeO_2), zinc oxide (ZnO), magnesium oxide (MgO), barium oxide (BaO), lead oxide (PbO), cesium carbonate (Cs_2CO_3), rubidium carbonate (Rb_2CO_3), potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3) and lithium carbonate (Li_2CO_3). Calculated quantities of chemicals were mixed in a glass dish and melted in an electric furnace at 900 °C for 1 h using an alumina crucible. Each melt was cast into a preheated aluminium mould with a size of 18 × 13 × 13 mm. Subsequently, it was removed from the mould and transferred to a furnace for annealing process at a temperature from 270 to 380 °C depending on the glass composition. The glass density was measured by Archimedes method, weighed in air, and deionized water was used as immersion liquid. The chemical durability of glasses with dimensions 5 × 5 × 5 mm was evaluated from the weight loss in boiling deionized water at 100 °C during 1 h. The transition temperature of glasses (T_g) and the coefficient of thermal expansion (CTE) were carried out using a thermo-mechanical analyzer (TA Instruments, TMA 2940) at a heating rate of 10 °C/min in the 20–380 °C temperature range. All samples were cut and then polished to about 1 mm thick slabs for different optical measurements. The transmission spectra were measured using two different spectrophotometers (Carry 500 UV–vis–NIR and Spectrum BX FTIR from Perkin Elmer) in the ranges from 300 to 2000 nm and from 2000 to 8000 nm, respectively. The refractive indices of the samples were measured at 632.8 nm and 1550 nm by prism coupler (Metricon, Model 2010). The third-order nonlinear optical susceptibility was studied using the THG-maker fringes technique at near infrared wavelengths.

3. Results and discussion

3.1. Coefficient of thermal expansion (CTE) and glass transition temperature (T_g)

Low glass transition temperature, high viscosity and low thermal expansion are desirable for a good fiber optic preparation. These parameters could be changed with the glass composition, increased or decreased, by introducing the right modifiers. A representative measured thermal expansion and T_g curve for glasses is shown in Fig. 1. The coefficient of thermal expansion was obtained

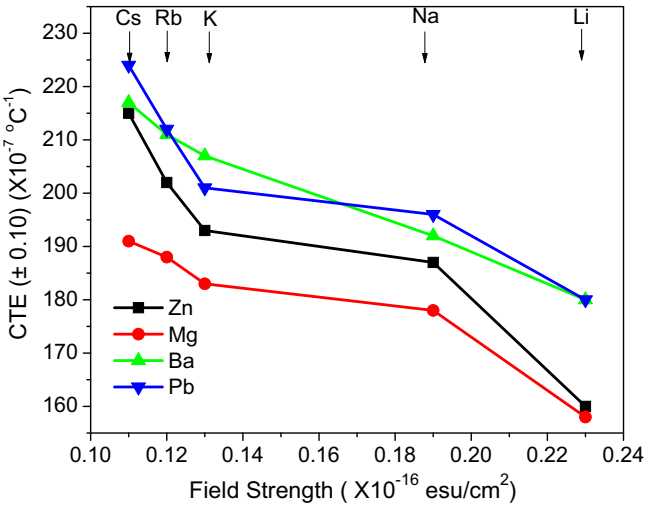

Fig. 2. Coefficient of thermal expansion of tellurite glasses composition.

from the slope in the 30–300 °C temperature range, while the glass transition temperature corresponds to the point where changes slope. The behavior of CTE for the 20 glasses is observed in Fig. 2, and the complete values are listed in Table 2. These glasses were analyzed as a function of field strength calculated as $F_s = Z_c/(r_c + r_o)^2$, where Z_c is the valence of cation, r_c and r_o are the ionic radii of cation and oxygen, respectively. These values are in the range of 158–224 × 10^{-7} °C^{-1} showing a decreasing trend from Cs to Li through Rb, K and Na for all glasses. This behavior indicates that a large ionic radius, and then a decrease in the strength of cationic field result in the observed increase of the coefficient of thermal expansion. CTE is dominated by the interaction of cations with nonbridging oxygens [3]. Since Li has the highest cation field strength, it is expected that Li_2O–MO–TeO_2 glasses could provide the lowest thermal expansion. The obtained values of CTE reported in this work are below 200 × 10^{-7} °C^{-1}, lower than values measured from 50 to 200 °C reported in phosphate by other authors [23]. It is also influenced by the presence of intermediate. In this case, an increment of CTE with an increase of the molecular weight or atomic number of intermediate (Pb, Ba, Zn, Mg) was observed.

Table 2
Coefficient of thermal expansion (CTE), dissolution rate (DR), refractive index (n), density (ρ) and third-order nonlinear optical susceptibility ($\chi^{(3)}$) of various tellurite glasses compositions

Code	CTE (10^{-7} °C^{-1})	DR (10^{-7} g/cm^{2}min^{-1})	ρ (g/cm^3)	n ± 0.0005		$\chi^{(3)}$ (10^{-13} esu)
	±0.10	±0.001	±0.001	632.8 nm	1550 nm	±10%
T11	224	5.562	5.554	2.0626	2.0071	7.18
T12	212	3.734	5.490	2.0306	1.9758	5.52
T13	201	3.733	5.354	1.9919	1.9404	4.81
T14	196	1.88	5.454	1.9817	1.9306	5.04
T15	180	1.84	5.574	1.9706	1.9229	7.02
T21	215	3.725	4.984	1.9728	1.9276	6.86
T22	202	3.566	4.874	1.9337	1.8914	4.69
T23	193	2.813	4.736	1.9007	1.862	4.35
T24	187	1.882	4.806	1.8834	1.845	3.81
T25	160	1.806	5.079	1.8817	1.8432	4.05
T31	217	12.68	4.733	1.9375	1.8954	7.02
T32	211	9.312	4.625	1.9049	1.8637	6.11
T33	207	9.343	4.479	1.8729	1.835	4.06
T34	192	5.632	4.727	1.8663	1.8289	3.83
T35	180	3.761	4.794	1.8603	1.8251	4.02
T41	191	14.61	5.035	1.9379	1.8945	13.12
T42	188	11.37	4.928	1.8994	1.8611	4.80
T43	183	7.360	4.784	1.8718	1.8335	3.28
T44	178	5.603	4.990	1.8602	1.8225	3.10
T45	158	3.761	5.097	1.8598	1.8225	3.24

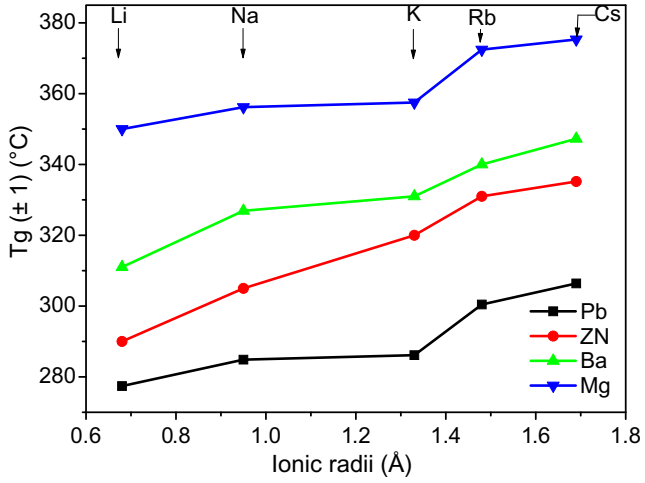

Fig. 3. Glass transition temperature (T_g) as a function of ionic radii.

The glass transition temperature (T_g) shows an opposite trend to thermal expansion for all samples, see Fig. 3. A monotonic increment from Li to Cs in ranges from 277 to 306 °C, 295 to 335 °C, 311 to 347 °C and 352 to 373 °C for series T1 (Pb), T2 (Zn), T3 (Ba) and T4 (Mg), respectively is observed. The increment was produced by the very large ionic radii and small field strength of alkali metals modifiers. When Cs was replaced by Li through Rb, K and Na, the ionic radii decrease and then the field strength becomes greater. Thus, the Li–O bonds in the glass network are stronger and then T_g will be increased. The relationship of T_g with intermediate ion is not completely clear. Apparently it increases by reducing the molecular weight; however, there is a different behavior between Ba and Zn suggesting the presence of an additional mechanism.

3.2. Chemical durability

Good chemical durability is a very important parameter to make high quality optical fiber. Under normal conditions of operation glasses should not exhibit any noticeable degradation caused by environment. For this reason, good chemical durability is a critical requirement. The chemical durability of R_2O–MO–TeO_2 glasses was determined from the measurements of dissolution rate (DR) in boiling water. A small value of DR indicates a good chemical durability, while a large value indicates poor chemical durability. Samples were cut and polished with a dimension of 5 × 5 × 5 mm for weight loss per surface area measurement. All samples under study were carefully weighed and placed in a baker with 200 ml of deionized boiling water. After 1 h, glasses were removed and washed with acetone, and were dried subsequently in a furnace at 80 °C for 1 h and weighed again. All measurements were made in duplicate and the averages of two values are shown in Table 2. The dissolution rate (DR) of glasses was calculated using the relation

$$DR = \Delta W/(S \cdot t), \quad (1)$$

where ΔW is the difference on initial and final weight, S is the total surface area of the cube and t is the immersion time of glasses in water. The behavior of DR as a function of field strength of alkali metals is shown in Fig. 4. DR for glasses decreases monotonically with the increment of field strength, from Cs to Li through Rb, K and Na. However, a specific trend as a function of field strength was not observed for network intermediate. DR decreases from Mg to Zn through Ba and Pb, but in all cases chemical durability was improved when Cs was replaced by Li. In fact, DR is 2.5, 3, 3.5 and 4 times bigger for R_2O–ZnO–TeO_2, R_2O–PbO–TeO_2, R_2O–BaO–TeO_2 and R_2O–MgO–TeO_2 glasses, respectively. Since Li has higher field strength and Li–O bonds are stronger, the chemical durability of Li_2O–MO–TeO_2 glass is higher.

3.3. Transmission spectra

Transmission spectra of all samples were measured over a spectral range from 0.3 to 2.5 μm and 2 to 8 μm, few representative spectra are shown in Fig. 5. All samples present good transparency in a range from 0.35 to 6.4 μm with very little changes depending on the glass composition. Fig. 4a shows the UV transmission cutoff of R_2O–PbO–TeO_2 glasses being centred around 360 nm. No significant changes were observed in the λ_{cutoff} with the replacement of alkali metals. Only a slight shift of 10 nm on λ_{cutoff} was observed by the substitution of different alkali metals and 25 nm for different intermediates. This indicates that λ_{cutoff} depends mostly on the network intermediate. Notice that these glasses have low UV trans-

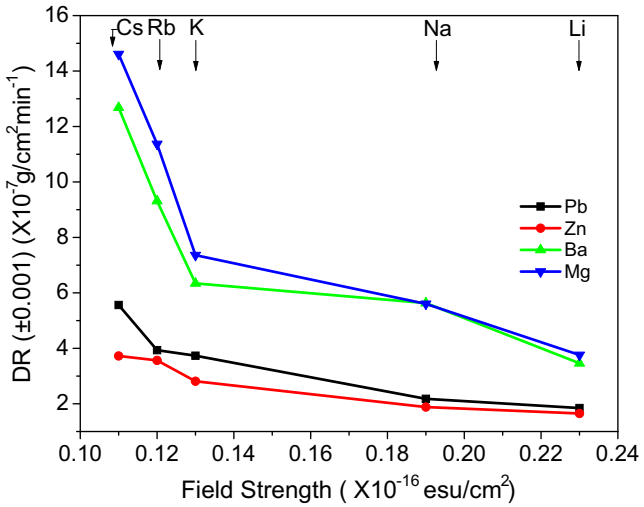

Fig. 4. Dissolution rate of R_2O–MO–TeO_2 glasses in deionized boiling water.

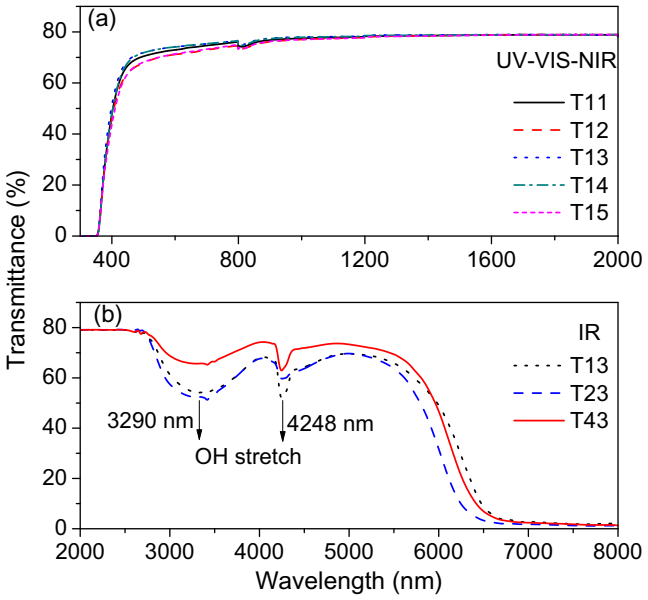

Fig. 5. Transmission spectra in a range of (a) 300–2500 nm and (b) 2000–8000 nm.

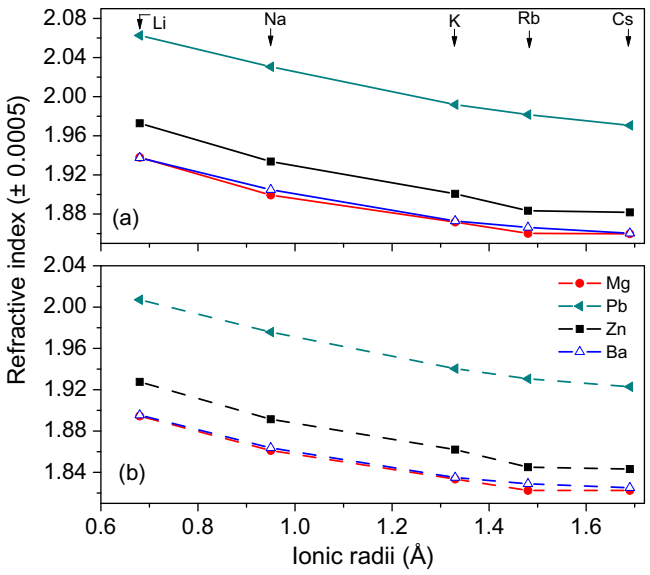

Fig. 6. Refractive index as a function of ionic radii for R_2O–MO–TeO_2 glasses at (a) 632.8 nm and (b) 1550 nm.

mission in comparison with phosphate and borate glasses indicating weak Te–O bond [24].

The cutoff in the IR range is shown in Fig. 4b. The λ_{cutoff} was shifted from 6.170 to 6.410 μm when Mg was replaced by Pb through Ba and Zn. That means, λ_{cutoff} was shifted to larger wavelength by increasing the molecular weight of the intermediate. Just by introducing the right network intermediator, a 240 nm broad bandwidth in the transmission spectra is observed. On the other hand, no significant changes were observed when the alkali metals were replaced one by one. This indicates that intermediate dependence of IR λ_{cutoff} is stronger than alkali metal. Fig. 4b shows a strong absorption band at approximately 3290 nm, which is associated to OH-group stretching vibrations, as well as to a weaker band at 4248 nm.

3.4. Refractive index and density

The refractive index is a critical parameter in the control of mode profile, which affects the performance of optical fiber amplifiers [25]. For this reason, it is necessary to know the effect of network modifiers introduction into tellurite glasses. The measured values of refractive indices at 632.8 nm and 1550 nm as the function of ionic radii are shown in Fig. 6. It can be seen that refractive index increases from Cs to Li for the four batches in ranges from 1.9705 to 2.0626, 1.8817 to 1.9728, 1.8603 to 1.9375 and 1.8598 to 1.9379 for R_2O–PbO–TeO_2, R_2O–ZnO–TeO_2, R_2O–BaO–TeO_2 and R_2O–MgO–TeO_2 glasses, respectively, see Table 2. The results show that the highest values of refractive index were obtained when lithium was incorporated into the tellurite glasses. The observed trend suggests an increment of refractive index with a decrement of the ionic radii or an increment of field strength. Notice that such effect depends on the intermediate ion being more pronounced for PbO and ZnO, but diminished for BaO and MgO. It is clear that by modifying the glass composition it is possible to increase or decrease the refractive index. Such dependence indicates the importance of the right glass composition of both modifiers and intermediate. The difference of refractive indices could be very useful as core and cladding glasses for optical fiber fabrication. However, core and cladding glasses must have similar thermal properties in order to avoid crystallization when preform is drawing. In our case, T22–T14, T34–T41 and T35–T43 samples have similar thermal properties (T_g and coefficient of thermal expansion) and also keep the difference of refractive indices that make those glasses ideal for optical fiber fabrication.

The linear refractive index (n) is related with the electronic polarizability (α_e) and molar volume (V_m) by the Lorentz–Lorenz equation [4]

$$n = \left(\frac{1 + 2\frac{4\pi N_A}{3}\frac{\alpha_e}{V_m}}{1 - \frac{4\pi N_A}{3}\frac{\alpha_e}{V_m}}\right)^{\frac{1}{2}}, \quad (2)$$

where N_A stands for Avogadro's number. This equation indicates that the refractive index increases as the term α_e/V_m increases. Since polarizability increases with the ion size, it is expected that for group IA of periodic table the refractive index should increase with the increasing atomic number from Li to Cs. However, the experimental data show an opposite trend, the refractive index increases from Cs to Li. Such behavior suggests that the molar volume increases faster than the electronic polarizability, and as a consequence the term α_e/V_m diminishes. This explains why the refractive index is larger when Li is incorporated into tellurite glass. Such behavior had been reported previously for phosphate glasses [4].

Fig. 7 shows the density for all samples under study. Those values are in the ranges from 5.35 to 5.75, 4.73 to 5.07, 4.78 to 5.09, 4.47 to 4.79 g/cm^3 for the series T1, T2, T3 and T4, respectively, see Table 2. It is observed that density decreases by reducing the ionic radii of the alkali metals, Li, Na and K. Such trend has been reported for phosphate and silicate glasses [10]. However, density increases with the introduction of Cs and Rb. The reason for this anomalous behavior is not clear at this stage. One possible explanation of this phenomenon is based on the fact that the decomposition temperature of Cs and Rb is lower than that of K, Na and Li. Probably, both Cs and Rb are decomposed and evaporated due to the high melting temperature used. Consequently, when the glass is solidified, Te–O and M–O bonds are larger than R–O bonds producing an increment on glass density. More experiments are in progress to elucidate this point.

3.5. Third-order nonlinearity

The third-order nonlinear optical susceptibility $\chi^{(3)}$ for MO–R_2O–TeO_2 glasses was measured by the well-known third har-

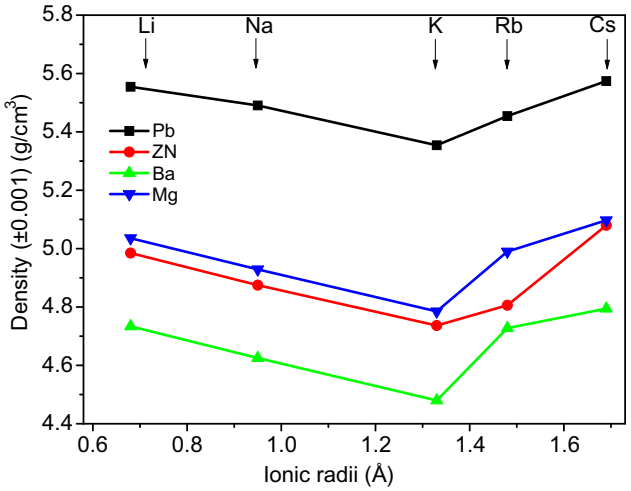

Fig. 7. Density of tellurite glasses introducing several modifiers.

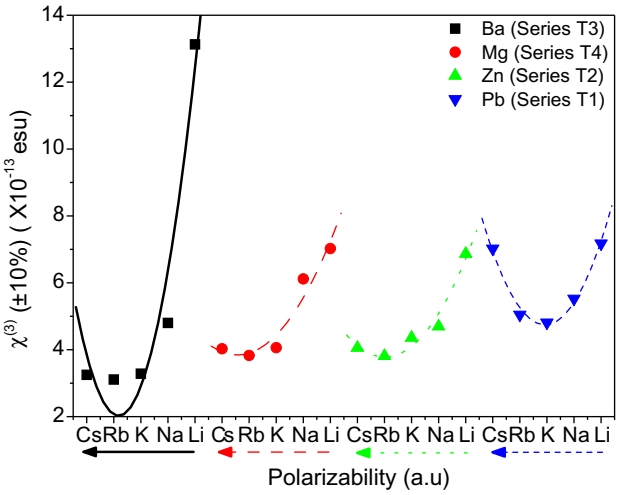

Fig. 8. Third-order nonlinear optical susceptibility $\chi^{(3)}$ for the R_2O–MO–TeO_2 glasses.

monic generation (THG) method [26–31] with nanosecond pulsed excitation at 1550 nm. In this method, $\chi^{(3)}$ was calculated from the THG output intensity measured as a function of the incident beam angle with respect to the normal of surface sample, details of the experimental setup can be found elsewhere [32]. $\chi^{(3)}$ was calculated by the expression

$$\chi^{(3)}_{\text{Sample}}(-3\omega;\omega,\omega,\omega) = \chi^{(3)}_{\text{SiO}_2}\frac{L_{\text{C,SiO}_2}}{L_{\text{C,Sample}}}\sqrt{\frac{I_{3\omega,\text{Sample}}}{I_{3\omega,\text{SiO}_2}}} \times \sqrt{\frac{T^3_{\omega,\text{SiO}_2}\cdot T_{3\omega,\text{SiO}_2}}{T^3_{\omega,\text{Sample}}\cdot T_{3\omega,\text{Sample}}}} \times \sqrt{\frac{n^3_{\omega,\text{Sample}}\cdot n_{3\omega,\text{Sample}}}{n^3_{\omega,\text{SiO}_2}\cdot n_{3\omega,\text{SiO}_2}}}. \quad (3)$$

Here, $L_{\text{C,Sample}}$ and $I_{3\omega,\text{Sample}}$ represent the coherence length and the intensity of the third harmonic generation for the sample, respectively. $L_{\text{C,SiO}_2}$ and $I_{3\omega,\text{SiO}_2}$ are the corresponding parameters for fused silica used as a standard sample. The value of $L_{\text{C,SiO}_2} = 14.7$ μm at 1550 nm was used for all calculation performed. $\chi^{(3)}_{\text{SiO}_2} = 3.1\times10^{-14}$ esu (dispersion of nonlinearities in fused silica was ignored) was used as a reference for nonlinear susceptibility. The coherent length of the sample $L_{\text{C,Sample}}$ was determined by $L_{\text{C,Sample}} = \frac{\lambda_\omega}{6(n_{3\omega}-n_\omega)}$, where λ_ω is the incident beam wavelength, $n_{3\omega}$ and n_ω represent the linear refractive indices at 517 nm and 1550 nm, respectively. $T_{3\omega}$ and T_ω represent the apparent transmittance including the reflection loss at the surface. The calculated values of the third-order nonlinear optical susceptibility are listed in Table 2, and the behavior as the function of polarizability is shown in Fig. 8. All samples under study present an increment of $\chi^{(3)}$ as polarizability and ionic radii decrease from K, Na and Li. Values range from 4.81 to 7.17×10^{-13} esu, 4.35 to 6.86×10^{-13} esu, 4.06 to 7.02×10^{-13} esu and 3.28 to 13.1×10^{-13} esu for series T1, T2, T3 and T4, respectively. These results are in good agreement with the data previously reported for various tellurite glass compositions. Those values are smaller than 8.2×10^{-13} esu and 12.8×10^{-13} esu measured at 1500 and 1900 nm, respectively [33–34]. Notice the little fluctuation of $\chi^{(3)}$ for Cs and Rb. Apparently, nonlinearity diminishes from K to Rb but increases for Cs. Such behavior is similar to that observed for density. The value obtained for Cs in T3 series is much larger than that obtained for other series. Probably, such deviation is associated with some surface irregularities of the sample that is well known to strongly affect the nonlinear calculation.

Since the linear refractive indices of tellurite glasses increase from Cs to Li (Section 3.4), it is expected that $\chi^{(3)}$ and the nonlinear refractive index (n_2) increase with such increment [35]. Unfortunately, it is not possible to establish a direct relationship between $\chi^{(3)}$ and n_2. However, preliminary results obtained by *z*-scan technique confirm such trend, i.e., an increment of $\chi^{(3)}$ produces an increment of n_2. Nonlinear refractive index is an important parameter to be considered in laser application in order to prevent spatial intensity fluctuations and self-focusing. In high power laser system, nonlinearity can produce high thermal lensing, beam quality degradation, reduction of the energy extraction efficiency and increase the risk of laser-induced damage [5,36–37]. On the other hand, because the power in optical amplifiers is lower than that in laser operation such nonlinear effect should be negligible. However, if n_2 is high such nonlinear effects must be considered. In general, n_2 should be as low as possible to avoid undesirable effects.

3.6. Conclusions

Based on the experimental results obtained from the systematic characterization of R_2O–MO–TeO_2 glasses it is concluded that optical, chemical and thermo-mechanical properties of tellurite glasses are strongly influenced by the introduction of alkali metals and network intermediate. The introduction of such ions modifies the glass network and then their properties. Some of those properties are improved but others are reduced. Then, it is necessary to make a compromise of desired properties and then to define the glass composition. Experimental results indicate that alkali metals with small ionic radii improve chemical (DR) and mechanical (α, T_g) properties. However, they also increase n and $\chi^{(3)}$ (and then n_2). The former is good for the spectroscopic properties in laser and amplifier application but nonlinear response induces a deleterious effect. The trend observed for the introduction of intermediate is more complicated. Lower thermal expansion coefficient was obtained for Zn and Mg, while better chemical durability corresponds to Pb and Zn. Lower refractive index was obtained for Mg and Ba. Although all intermediates under study present the same behavior, the minimum value was obtained for Ba. The R_2O–MO–TeO_2 glasses have a wide transmission range from 0.35 to 6.4 μm, from these results it has been established that UV and IR transmission λ_{cutoff} seem less sensitive to alkali metal than network intermediate. Based on all these results, it is suggested that R_2O–MO–TeO_2 glasses could be used in nonlinear optical devices because of their large third-order nonlinear optical susceptibility. Additionally they provide other properties such as high refractive index, good chem-

ical durability, wide transmission spectrum and low coefficient of thermal expansion.

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