THIRD-ORDER NONLINEAR OPTICAL PROPERTIES
AND LOW-FREQUENCY RAMAN SCATTERING OF MO-Nb₂O₅-TeO₂ GLASSES

T. Suhara¹, T. Hayakawa¹, M. Nogami¹, Ph. Thomas²

¹ Field of Advanced Energy Conversion, Department of Frontier Materials, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan
² Science des Procédés Céramiques et de Traitements de Surface (SPCTS), UMR 7315 CNRS, Faculte des Sciences, Universite de Limoges, 12, rue Atlantis, 87068 Limoges Cedex, France
E-mail: hayatomo@nitech.ac.jp

ABSTRACT

TeO₂-based glasses are known to have high third-order optical nonlinear properties and promising as nonlinear optical devices. In this study, the relationship between glass structures and third-order nonlinear optical properties $\mathbf{R} \mathbf{e} \chi^{(3)}$ in MO-Nb₂O₅-TeO₂ (M=Zn, Mg, Ca, Sr, Ba) glasses was investigated by femtosecond Z-scan and low-/intermediate-frequency Raman scattering. The structural correlation lengths $\sigma$ of the glasses studied were estimated from a boson peak in low-frequency Raman scattering spectra. The relationship between $\mathbf{R} \mathbf{e} \chi^{(3)}$ and the structural correlation length $\sigma$ was discussed. It was concluded that the longer correlation length $\sigma$ brought about the higher $\mathbf{R} \mathbf{e} \chi^{(3)}$ in MO-Nb₂O₅-TeO₂ glass.

Keywords: optical nonlinear properties, glass structures, nonlinear optical devices.

INTRODUCTION

Nonlinear optical (NLO) glasses are expected to be applied to active photonic devices in optical telecommunications, such as ultrafast optical switching, frequency converters, NLO fibers, and laser optics. Compared with conventional glasses based on SiO₂, B₂O₃, and P₂O₅ etc, as a main component, TeO₂-based glasses [1-8] are peculiar for their excellent transparency from visible to infrared region, chemical durability, low-melting points, high refractive index (≥2.0) and low phonon energies (600-700 cm⁻¹). Tellurium dioxide (or tellurite, TeO₂) is difficult to be vitrified alone, which is quite different from other glass systems. However, once other metal oxides are doped, amorphous network system of TeO₂ can be obtained at a usual cooling rate with a considerably wide range of constituents. In the past decades, many researchers paid attention to TeO₂-based binary glass systems (e.g. alkali tellurite, ZnO-TeO₂, PbO-TeO₂, TiO₂-TeO₂, Nb₂O₅-TeO₂). It has been known that several TeO₂ glass doped with heavy metal oxide which can be easily polarized (Bi³⁺, Pb²⁺) or with empty d orbital (Ti⁴⁺, Nb⁵⁺) have higher third-order NLO properties than other TeO₂ glasses. Recently, it is a trial to extend the glass forming area from binary to ternary systems with heavy metal oxide or empty d orbital ion (e.g. TiO₂-Nb₂O₅-TeO₂, Bi₂O₃-Nb₂O₅-TeO₂). It was reported that co-doping ZnO and Nb₂O₃ could improve NLO properties of TeO₂ glass, and so a glass system of ZnO-Nb₂O₅-TeO₂ is here picked up. In this paper, we briefly introduce our recent findings for nonlinear properties and glass structures of divalent metal oxide (MO: M = Zn, Mg, Ca, Sr, Ba) doped Nb₂O₅-TeO₂ [9-11]. And the low-frequency Raman scattering for the estimation of the correlation lengths $\sigma$ of
glass structures is analyzed and the relationship between \( \sigma \) and \( \text{Re} \chi^{(3)} \) shall be discussed.

**EXPERIMENTAL**

The glass samples were prepared using \( \text{TeO}_2 \), \( \text{Nb}_2\text{O}_5 \) and \( \text{MO} \) (M=Zn, Mg, Ca, Sr, Ba) powders. The mixture was melted at 1000°C for 20 min. in an alumina crucible in an ambient atmosphere and quenched into a stainless ring placed on a brass stage warmed at \( \sim 130^\circ\text{C} \) to obtain pellet-type samples with 10 mm in diameter and 1 mm in thickness. The quenched glasses were systematically annealed at a temperature 50°C below the respective glass transition temperature (\( T_g \)) for 10 h in order to release thermal stresses resulting from the quenching. In \( \text{Nb}_2\text{O}_5\text{-TeO}_2 \) binary system, 20 mol % of \( \text{Nb}_2\text{O}_5 \) contents was the maximum to obtain uniform and transparent glass samples without vitrification. Therefore, the content of \( \text{Nb}_2\text{O}_5 \) in \( \text{MO-Nb}_2\text{O}_5\text{-TeO}_2 \) glass was fixed to be 20 mol %. To evaluate \( \text{Re} \chi^{(3)} \) using Z-scan technique, a femtosecond (fs) pulse from regenerative Ti: Sapphire laser (Spectra Physics, Hurricane) were used at 800 nm at 1kHz repetition rate and with \( \sim 90 \) fs pulse duration [10,11].

Also, we carried out some characterizations (thermal analysis using DTA-TG, linear refractive index, density) and glass structures of \( \text{TeO}_2 \)-based glasses in interest were measured using Raman spectrophotometer (JASCO, NRS-2000). An excitation source was Ar+ laser with 514.5 nm. For observing a boson peak, the incident light was polarized in a direction perpendicular to the scattering plane while the scattered light was analyzed in cross-polarization configuration.

**RESULTS AND DISCUSSION**

Fig. 1 is a Z-scan curve of \( 4\text{MgO-20Nb}_2\text{O}_5\text{-76TeO}_2 \) glass. The real part of \( \chi^{(3)} \) of glasses studied was estimated from a difference of transmittance \( \Delta T_{pv} \) at a peak and valley [10,11]. Fig. 2 shows \( \text{Re} \chi^{(3)} \), measured in 800 nm femtosecond laser for \( 20\text{Nb}_2\text{O}_5\text{-80TeO}_2 \) and \( 2\text{MO-20Nb}_2\text{O}_5\text{-78TeO}_2 \). \( \text{Re} \chi^{(3)} \) of the glasses studied was ranged from 3.0x10\(^{-13}\) to 4.41x10\(^{-13}\) esu [11,12]. Noticeably, regardless of the type of MO, xMO-\( 20\text{Nb}_2\text{O}_5\text{-80TeO}_2 \) glasses had higher \( \text{Re} \chi^{(3)} \) than \( 20\text{Nb}_2\text{O}_5\text{-80TeO}_2 \) glass even if \( \text{TeO}_2 \) content was decreased. The real part of \( \chi^{(3)} \) for \( \text{ZnO-doped \ Nb}_2\text{O}_5\text{-TeO}_2 \) glasses [13] was the highest at 2 mol % and higher than those of the other glasses studied.

A baseline-corrected Raman spectrum of \( 20\text{Nb}_2\text{O}_5\text{-80TeO}_2 \) glass is shown in Fig. 3. This spectrum could be analyzed into seven Gaussian bands. The ratios of the respective \( \text{TeO}_x\text{-TeO}_y \) linkage (A: 400cm\(^{-1}\), B: 440cm\(^{-1}\)) and structural units (\( \text{TeO}_4 \)(C: 600 cm\(^{-1}\), D: 660 cm\(^{-1}\)), \( \text{TeO}_5 \)(E: 730 cm\(^{-1}\)), \( \text{TeO}_6 \)(F: 780 cm\(^{-1}\)) \( \text{NbO} \) in three-dimensional \( \text{NbO}_x \) clusters (G: 850 cm\(^{-1}\)) in \( \text{MO-Nb}_2\text{O}_5\text{-TeO}_2 \) glasses were evaluated using integral of the corresponding bands which were obtained by the deconvolution with Gaussian functions [11,14]. The total of the integrals was normalized ([\( \text{TeO}_4 \] + [\( \text{TeO}_5 \] + [\( \text{TeO}_6 \] = 100 %). The relationship between these ratios and \( \text{ZnO} \) contents in \( \text{ZnO-Nb}_2\text{O}_5\text{-TeO}_2 \) glasses was depicted in Fig. 4. It can be seen that with an increase of
the ZnO content, the ratio of TeO$_4$ unit and Te - O$_{ax}$ - Te linkage decreased and that of TeO$_{3+1}$ unit increased. In contrast, the ratios of TeO$_5$ unit and Nb-O were constant, independent of the ZnO content. These results showed that the doping of ZnO allows TeO$_4$ units to be converted to TeO$_{3+1}$ units [11]. In the other MO-doped glasses, the same transformation of the glass structures was observed. With these results, a glass network model in MO-Nb$_2$O$_5$-TeO$_2$ glass was discussed. It is widely accepted that doping MO toward TeO$_2$ glass converted TeO$_4$ unit to TeO$_3$ (terminal) units and broken Te- O$_{ax}$ - Te linkage in MO-TeO$_2$ glass. Since nonlinear polarizability of TeO$_3$ unit is lower than that of TeO$_4$ unit, Re$\chi''$ of MO-TeO$_2$ glass was decreased. In this research, it was revealed that doping Nb$_2$O$_5$ inhibited an increasing TeO$_3$ unit and converted TeO$_4$ to TeO$_{3+1}$ units. From the above consideration, it was found that Nb$^{5+}$ acted as a network former. Thus, we previously proposed a glass network model which consists of MO$^{2+}$, (NbO$_2$)$_7$ and TeO$_{3+1}$ unit for MO-Nb$_2$O$_5$-TeO$_2$ glasses [11]. This glass network model in MO-Nb$_2$O$_5$-TeO$_2$ was shown in Fig. 5.

Depolarized Raman scattering spectra was depicted in Fig. 6. In the glasses studied, a boson peak could be observed at approximately 45 cm$^{-1}$ for the respective glasses in interest. It is reported that “boson peak” was attributed to the vibration of medium-ranged structure in glass network. According the Martin and Brenig model [15], the cross-over can be characterized by structural correlation length $\sigma$. It is defined by the frequency of a boson peak $\omega_{BP}$ and the sound velocity $V_s$ in Eq.(1).

$$\sigma = \frac{V_s}{2\pi \omega_{BP}}$$  \hspace{1cm} (1)
CONCLUSIONS

In summary, the relationship between the glass structures and third-order nonlinear optical susceptibilities $\text{Re} \chi^{(3)}$ in MO-Nb$_2$O$_5$-TeO$_2$ (M=Zn, Mg, Ca, Sr, Ba) glasses was investigated. From the analysis of glass structures used by Raman scattering spectra, the addition of MO allowed TeO$_4$ units to be converted Te$_3$O$_7$ units. Moreover, it was suggested the glass network model consisted of M$^{2+}$, (NbO)$_6^5^-$ and TeO$_3$+ unit in MO-Nb$_2$O$_5$-TeO$_2$ glass. From the observation of the boson peak in low-frequency Raman scattering spectra, the correlation length $\sigma$ was estimated. The correlation length $\sigma$ of ZnO-Nb$_2$O$_5$-TeO$_2$ glass was the longest among the 2 mol% MO-doped Nb$_2$O$_5$-TeO$_2$ glasses. As discussed with the data of $\text{Re} \chi^{(3)}$ and correlation length $\sigma$, it was concluded that the longer correlation length $\sigma$ brought about the higher $\text{Re} \chi^{(3)}$ in MO-Nb$_2$O$_5$-TeO$_2$ glass.

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REFERENCES

12. The previous $R_{ex}$ values were over-estimated and should thus be corrected as seen in this article.