Inorganic Photonic Materials — Preparation and Third Order Non-Linear Optical Properties

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Third order nonlinear optical properties of various non-conventional glasses such as TeO_2-, Ga_2O_3-, Sb_2O_3-based glasses have been examined in relation to glass structure which was studied by using a number of experimental techniques (X-ray, neutron diffraction, MAS-NMR, IR, Raman Spectroscopy etc.). In addition, coating films of transition metal oxides and metal oxides containing metal fine particles have been prepared by the sol-gel method and subjected to various optical characterizations by focusing especially on the third order nonlinear optical susceptibility, $\chi^{(3)}$. It is found that α-Fe_2O_3 exhibits the highest $\chi^{(3)}$ value of 5.8×10^{-11} esu among the inorganic materials studied so far.

Keywords: Inorganic photonic materials/ Glasses/ Thin films/ Sol-gel method/ Glass Structure/ Third order nonlinear optical susceptibility $\chi^{(3)}$

The advent of optical glass fibers has made high-speed and long-distance telecommunication possible, leading to the present highly sophisticated modern media. The present optical telecommunication system is, however, limited by the processing speed of electronics currently used. Nonlinear optical (NLO) devices will overcome this problem because they can switch and process signal in a time scale of 10^{-15} s inaccessible to electronics (10^{-12} s) without converting it into electronic form. Moreover, it is anticipated that the ultrahigh-speed "optical computer," in which optical switching devices are utilized, will replace the conventional, semiconductor-driven computer in the near future. Therefore, it is urgently necessary to develop nonlinear optical materials which can be used as NLO devices. In our laboratory, two types of inorganic NLO materials are studied: (1) non-conventional glasses by melting method, (2) coating films formed on a glass substrate by the sol-gel method. We will present several representative results currently obtained in the following.

A thin plate of TeO_2 glass of $5.0\times4.0\times0.25\,mm^3$ in size, which was large enough for various optical measurements, was obtained by a rapid quenching method. The linear refractive index was measured as a function of wavelength from 486.1 to 1000 nm. The refractive index at 486.1 nm was as high as 2.239. The optical energy band gap was estimated as 3.37 eV from the optical absorption spectrum. The third-order nonlinear optical susceptibility, $\chi^{(3)}$, was determined by the third-harmonic generation (THG) method. The $\chi^{(3)}$ value was as high as 1.4×10^{-12} esu, about 50 times as large as that of SiO_2 glass. The results are discussed based on Lines' model in which an influence of cationic empty *d*-orbital on the nonlinear properties is taken into

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Scope of research

Two main subjects have been studied in this laboratory. The first is to develop a new family of glasses which do not contain so-called glass formers such as SiO_2, P_2O_5, B_2O_3 and so on. Relationships between glass formation and structure, and then relationships between structure and properties, especially nonlinear optical properties, are tried to be established. The second is to synthesize new functional inorganic thin films by the sol-gel method which is known as one of the most advantageous low temperature synthesis processes. Our attention is focused especially on the nonlinear optical properties of these films.

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Rutile and anatase thin films have been prepared by sol-gel method using $Ti(OC_3H_7^i)_4$. Third-order nonlinear optical properties of both TiO_2 thin films have been investigated by the third-harmonic generation (THG) method and the effect of the polymorph of TiO_2 on the third-order nonlinear optical susceptibility, $\chi^{(3)}$, has been examined. The measured $\chi^{(3)}$ values of rutile and anatase thin films were 1.4×10^{-12} and 9.7×10^{-13} esu, respectively. The $\chi^{(3)}$ values corrected for the porosity of the film were 4.0×10^{-12} (rutile) and 2.4×10^{-12} esu (anatase), which are about 100 times as high as that of SiO_2 glass used as standard sample (2.8×10^{-14} esu). The measured and corrected $\chi^{(3)}$ values were discussed in comparison with those calculated on the basis of several models.

The third-order nonlinear optical properties of sol-gel derived transition metal oxide, V_2O_5, Nb_2O_5 and Ta_2O_5, thin films have been investigated by the third-harmonic generation method and the effect of the metal-oxygen bond length on the third-order nonlinear optical susceptibility, $\chi^{(3)}$, has been examined. The $\chi^{(3)}$ values of V_2O_5, Nb_2O_5 and Ta_2O_5 thin films were 1.1×10^{-11}, 1.3×10^{-12} and 6.1×10^{-13} esu, respectively, which corresponds to an increase of the average bond length, l_b, in the order of V-O (l_b=0.183 nm), Nb-O (l_b=0.200 nm) and Ta-O (l_b=0.204 nm). The present and previous results indicate that $\chi^{(3)}$ of these transition metal oxides with the empty d orbitals is dominated mainly by the metal-oxygen bond length rather than the valence of metal cation. It is predicted on the basis of Lines' model that transition metal oxides with the shortest l_b exhibit the highest $\chi^{(3)}$ while non-transition metal oxides with the longest l_b do the highest $\chi^{(3)}$.

The third-order nonlinear optical properties of sol-gel α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4 thin films have been investigated by the third-harmonic generation (THG) method. Especially, the effects of the valence and coordination number of Fe ions on the third-order nonlinear optical susceptibility, $\chi^{(3)}$, have been examined. The $\chi^{(3)}$ values of α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4 thin films were 5.8×10^{-11}, 2.1×10^{-11} and 4.0×10^{-10} esu, respectively, which are the highest values among inorganic oxides reported so far. It was considered that $\chi^{(3)}$ of α-Fe_2O_3 and γ-Fe_2O_3 was enhanced by the pair excitation process involving the simulation of magnetically coupled two neighboring Fe^{3+} ions while $\chi^{(3)}$ of Fe_3O_4 by both one- and three-photon resonances. The higher second-hyperpolarizability, γ ($Fe_{x/y}O$), was obtained when the valence of Fe ions is 3+ rather than 2+ and octahedrally rather than tetrahedrally coordinated by oxygens.

Third-order nonlinear optical properties of sol-gel derived $FeTiO_3$ thin films have been investigated by the third-harmonic generation (THG) method, and the effect of valence of Fe ions on the third-order nonlinear optical susceptibility, $\chi^{(3)}$, has been examined. The $\chi^{(3)}$ value of $FeTiO_3$ thin film was 3.3×10^{-12} esu, which is comparable to those or TiO_2 polymorphs (rutile and anatase) but one order of magnitude lower than of α-Fe_2O_3. Second-hyperpolarizability per $Fe^{2+}O$ formula unit, γ ($Fe^{2+}O$), was one fourth to one third of γ ($Fe_{2/3}{}^{3+}O$) and about four times as large as γ ($Ti_{1/2}{}^{4+}O$), indicating that the $\chi^{(3)}$ value of $FeTiO_3$ may be dominated by the γ ($Fe^{2+}O$) rather than γ ($Ti_{1/2}{}^{4+}O$).

The preparation process of single phase Pb ($Fe_{1/2}Nb_{1/2}$)O_3 (PFN) perovskite films on glass substrates by sol-gel method has been investigated and several optical properties of the resultant transparent PFN films have been examined. The refractive index at 633 nm of PFN perovskite films is as large as 2.409, which is larger than $Pb_3Nb_4O_{13}$ pyrochlore films by 0.14–0.16 at any wavelength. The $\chi^{(3)}$ of PFN films is estimated as 7.5×10^{-12} esu, which is the second highest value among oxides so far obtained. The $\chi^{(3)}$ of pyrochlore films is estimated as 2.8×10^{-12} esu, which is one-third as small as that of PFN films.

Silica coating films of 0.5–0.7 mm thickness doped by gold metal particles were prepared by heating gel coating films obtained from solutions of acid-catalyzed methyltriethoxysilane (MTES) and tetraethoxysilane (TEOS) mixture containing chlorauric acid tetrahydrate. Transparent coating films with deep blue, red, and purple colors were obtained. Changes in size and shape of the gold particles with the MTES content were observed. Lower MTES contents gave bigger and non-spherical particles, while higher MTES contents produced smaller and more spherical particles with a more uniform size distribution. The effect of heat-treatment temperature on the shape, size, and size distribution of the metallic gold particles was also studied.

References

1. Yoko T, Hashimoto T and Ishibashi K, *NEW GLASS*, **9**, 16–22 (1994) [in Japanese].
2. Hashimoto T, Yoko T and Sakka S, *Bull. Inst. Chem. Res., Kyoto Univ.*, **71**, 420–429 (1994).
3. Hashimoto T, Yoko T and Sakka S, *Bull. Chem. Soc. Jpn.*, **67**, 653–660 (1994).
4. Kim S H, Yoko T and Sakka S, *J. Am. Ceram. Soc.*, **76**, 2486–90 (1993).
5. Hashimoto T, Yoko T and Sakka S, *J. Ceram. Soc. Jpn.*, **101**, 52–56 (1993).
6. Hashimoto T and Yoko T, *Applied Optics*, in press.
7. Hashimoto T, Yamada T and Yoko T, submitted to *Phys. Rev. B.*
8. Innocenzi P, Kozuka H and Sakka S, *J. Sol-Gel Sci. Techn.*, **1**, 305–318 (1994).