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 TeO₂-, Ga₂O₃-, Sb₂O₃-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 $a$-Fe₂O₃ exhibits the highest $\chi^{(3)}$ value of $5.8 \times 10^{-11}$ 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 TeO₂ glass of $5.0 \times 4.0 \times 0.25$ 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 $1.4 \times 10^{-12}$ esu, about 50 times as large as that of SiO₂ 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 account.
account.

Rutile and anatase thin films have been prepared by sol-gel method using Ti(O\(_2\)C\(\text{H}_3\))\(_4\). 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 \(1.4 \times 10^{-12}\) and \(9.7 \times 10^{-13}\) esu, respectively. The \(\chi^{(3)}\) values corrected for the porosity of the film were \(4.0 \times 10^{-12}\) (rutile) and \(2.4 \times 10^{-12}\) esu (anatase), which are about 100 times as high as that of SiO\(_2\) glass used as standard sample (\(2.8 \times 10^{-14}\) 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\(_2\)O\(_5\), Nb\(_2\)O\(_5\) and Ta\(_2\)O\(_5\), 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\(_2\)O\(_5\), Nb\(_2\)O\(_5\) and Ta\(_2\)O\(_5\) thin films were \(1.1 \times 10^{-11}\), \(1.3 \times 10^{-12}\) and \(6.1 \times 10^{-13}\) esu, respectively, which corresponds to an increase of the average bond length, \(b_o\), in the order of V-O (\(b_o=0.183\) nm), Nb-O (\(b_o=0.200\) nm) and Ta-O (\(b_o=0.204\) 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 \(b_o\) exhibit the highest \(\chi^{(3)}\) while non-transition metal oxides with the longest \(b_o\) do the highest \(\chi^{(3)}\).

The third-order nonlinear optical properties of sol-gel derived \(\alpha\)-Fe\(_2\)O\(_3\), \(\gamma\)-Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\) 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 \(\alpha\)-Fe\(_2\)O\(_3\), \(\gamma\)-Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\) thin films were \(5.8 \times 10^{-11}\), \(2.1 \times 10^{-11}\) and \(4.0 \times 10^{-10}\) esu, respectively, which are the highest values among inorganic oxides reported so far. It was considered that \(\chi^{(3)}\) of \(\alpha\)-Fe\(_2\)O\(_3\) and \(\gamma\)-Fe\(_2\)O\(_3\) was enhanced by the pair excitation process involving the simulation of magnetically coupled two neighboring Fe\(_{\text{3+}}\) ions while \(\chi^{(3)}\) of Fe\(_3\)O\(_4\) by both one- and three-photon resonances. The higher second-hyperpolarizability, \(\gamma\) (Fe\(_{\text{3+}}\)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 \(3.3 \times 10^{-12}\) esu, which is comparable to those or TiO\(_2\) polymorphs (rutile and anatase) but one order of magnitude lower than of \(\alpha\)-Fe\(_2\)O\(_3\). Second-hyperpolarizability per Fe\(_{\text{3+}}\)O formula unit, \(\gamma\) (Fe\(_{\text{3+}}\)O), was one fourth to one third of \(\gamma\) (Fe\(_{\text{2+}}\)O) and about four times as large as \(\gamma\) (Ti\(_{\text{4+}}\)O), indicating that the \(\chi^{(3)}\) value of FeTiO\(_3\) may be dominated by the \(\gamma\) (Fe\(_{\text{3+}}\)O) rather than \(\gamma\) (Ti\(_{\text{4+}}\)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\(_2\)Nb\(_2\)O\(_9\) pyrochlore films by 0.14-0.16 at any wavelength. The \(\chi^{(3)}\) of PFN films is estimated as \(7.5 \times 10^{-12}\) esu, which is the second highest value among oxides so far obtained. The \(\chi^{(3)}\) of pyrochlore films is estimated as \(2.8 \times 10^{-11}\) 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
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