NON LINEAR OPTICAL PROPERTIES OF BOROPHOSPHATE GLASSES

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Abstract The non linear optical properties of glasses are investigated with the object of potential applications as optical devices e.g. amplification and modulation of light, parametric frequency conversion, ultra-fast switching etc. By combining structural, optical and theoretical studies the origin of the third-order optical response has been determined in sodium calcium borophosphate glasses containing increasing proportion of TiO_2 or Nb_2O_5 . The values of the third-order susceptibility $\chi^{(3)}$ can be analysed on the basis of the bond orbital theory and are directly related to the Ti/Nb d-orbital contributions. For the richest titanium and niobium glasses the clustering of TiO_n ($n = 5,6$) or NbO_6 entities tends to increase leading to an enhancement of the non linear index n_2 . More recently Second Harmonic Generation (SHG) has been observed when these glasses were subjected to a dc bias of 3kV at 300°C. The close examination of the glasses surfaces before and after poling brings new ideas about the microscopic origin of this phenomenon.

INTRODUCTION

Non-linear optical properties of transparent materials are at this time the focus of growing interest for elaboration of all-optical devices, such as photonic modulators, optical data storage and telecommunication, or for the spectral extension of laser sources¹. The recent discovery of Second Harmonic Generation (SHG) in glasses after poling treatment (the glass being inserted between two electrodes and submitted to high d.c. field) and/or under high energy radiation induces new development related to new functional integrated devices^{2,3}. Basically, the nonlinear optical properties of materials under an electromagnetic field E result from the generation of a polarisation P , which can be expressed as a power series in E : $P = \chi^{(1)} + \chi^{(2)} E.E + \chi^{(3)} E.E.E + \dots$ where $\chi^{(1)}$ is the linear susceptibility which accounts for the linear optical index, $\chi^{(2)}$ (responsible for SHG, $\chi^{(2)} = 0$ in glasses) and $\chi^{(3)}$ (responsible for nonlinear indices n_2)

correspond respectively to the second and third order nonlinear susceptibilities. The choice of the glass composition is dictated by the necessity of increasing n_2 but various other parameters must be considered e.g. irradiation damage threshold, ability to device realization such as wave-guides or fiber etc. From theoretical considerations⁴ and previous experiments¹ the intensity of n_2 increases with the introduction of d^0 ions (Ti^{4+} , Nb^{5+}) giving rise to high hyper-polarizable (Ti-O) n or (Nb-O) n entities. Moreover, the third order nonlinearity has been involved in the SHG mechanism through a coupling with the internal dc field generated inside the glass during poling^{2,3}. The present paper reviews recent results obtained for glasses with the following compositions (1-y) [0.95 NaPO₃, 0.05 Na₂B₄O₇] y TiO₂ (resp. Nb₂O₅) and (1-y) [0.9 Ca(PO₃)₂, 0.1 CaB₄O₇] y Nb₂O₅. The great stability of the sodium or calcium borophosphate matrix glasses allowed the introduction of large quantities of highly nonlinear TiO₂ and Nb₂O₅ oxides^{5,6}.

- (i) The $\chi^{(3)}$ values will be explained by coupling a structural investigation with a theoretical analysis by applying to glasses the bond orbital theory of M. E. Lines⁴.
- (ii) The origin of the SHG observed in some of these glasses submitted to a poling treatment will be discussed after a detailed investigation of the glass surfaces in contact with the electrodes.

EXPERIMENTAL PROCEDURE

The elaboration procedures for these glasses (classical melting of mixed oxides, air quenching and annealing) have been previously described⁵⁻⁷.

The linear and nonlinear indices have been measured by the use of a Mach-Zehnder interferometer^{8,9}. The laser source is a TiSa oscillator (resp. an OPO pumped by a TiSa oscillator) delivering polarized pulses of 150fs at 840nm (resp. 1.5 μ). The SH signal is measured in transmission through the poled calcium borophosphate glasses (poling conditions: d.c. bias=3kV, T=300°C during one hour). A TiSa oscillator (resp. Nd:YAG laser) is used for measurements at around 800nm (resp. 1.06 μ).

Structural characterizations were obtained by RAMAN, XAFS, XPS and FTIR spectroscopies. RAMAN, XAFS and XPS experimental analysis have been largely described^{7,10,11}. FTIR analysis has been used for poled calcium borophosphate

characterization: IR reflectance experiments were performed using an external reflection attachment (Grosegy, Specoc) at an angle of incidence of 12°. The extinction coefficient can be calculated from the reflectance spectra by the Kramers-Kronig analysis. Structural modifications after poling can be evidenced by calculating the subtraction between the poled anode or cathode face reflectance signal and the corresponding unpoled face signal.

RESULTS AND DISCUSSION

(i) Nonlinear indices and $\chi^{(3)}$ measurements at around 840nm and 1.5 μ are given on table 1. For each wavelength, the nonlinear efficiency is increasing with the ratio of Nb₂O₅ or TiO₂. This was effectively expected for d⁰ cations like Nb⁵⁺ and Ti⁴⁺ are well-known to polarize electronic clouds of oxygen in metal-ligand bonding formation⁴. Contrary to other glass systems containing niobium and titanium oxides, $\chi^{(3)}$ is not linear with the concentration of metallic cations in the glass but an enhancement of the nonlinear efficiency is observed (FIGURE 1.a, 1.b). This allowed our borophosphate glasses to reach an efficiency comparable to the commercial SF59 for the largest concentration in niobium. The theory of LINES has been successfully extended to our glasses by the use of Ti-O and Nb-O bonding parameters⁴ related to RAMAN and XAFS structural characterizations of metal-oxygen sites in glasses¹⁰⁻¹¹. Experimental macroscopic linear and nonlinear indices are in accordance with the calculated values using the Lines parameters, in so far oxygenated sites are isolated in the glass. An enhancement of the nonlinear $\chi^{(3)}$ response for the highest metal concentrations is observed when compared to the model⁸ (FIGURE 1.a, 1.b). It has been related to the formation of KTP-like Ti—O-Ti chains or three dimensional Nb-O framework^{8,10,11}.

(ii) SHG has been evidenced in poled calcium borophosphate glasses⁷ (table 2). After optimization of the glasses efficiency, the $\chi^{(3)}$ value cannot clearly be involved in the glass response which remains inferior to the Vitreosil or Herasil silica glass response. The nonlinearity has been proved to be localized near the surfaces in contact with electrodes during the poling treatment⁷, whereas an accumulation of sodium cations to the cathodic surface has been unambiguously observed by XPS spectroscopy¹².

TABLE 1 Nonlinear index results

compound	Wavelength: 840 nm			Wavelength: 1.5 μ		
	n_0 ± 0.02	n_2 $10^{19} \text{m}^2/\text{W}$ $\pm 10\%$	$\chi^{(3)}$ $10^{21} \text{V}^2/\text{m}^2$ $\pm 10\%$	n_0 ± 0.02	n_2 $10^{19} \text{m}^2/\text{W}$ $\pm 10\%$	$\chi^{(3)}$ $10^{21} \text{V}^2/\text{m}^2$ $\pm 10\%$
BPNa*-13.9%TiO ₂	1.59	1.6	0.8			
BPNa-26.3%TiO ₂	1.65	3.0	1.4	1.65	1.08	0.52
BPNa-33.3%TiO ₂	1.72	4.1	2.2	1.72	1.62	0.85
BPNa-42.2%TiO ₂	1.80	6.9	4.0	1.75	2.23	1.21
BPNa-11.3%Nb ₂ O ₅	1.61	2.2	1.0			
BPNa-30%Nb ₂ O ₅ **				1.77	2.06	1.14
BPNa-37.0%Nb ₂ O ₅	1.84	5.2	3.1			
BPNa-43.0%Nb ₂ O ₅	1.96	8.0	5.4			
BPNa matrix glass	1.48	0.9	0.4			
BPCa* matrix glass	1.56	0.86	0.37	1.57	0.05	0.02
BPCa-20%Nb ₂ O ₅ **	1.67	2.4	1.2	1.66	1.61	0.79
BPCa-30%Nb ₂ O ₅ **	1.76	3.8	2.1	1.71	2.35	1.21
Herasil silica glass	1.46	0.72	0.27	1.47	0.12	0.05
SF59	1.97	9.0	6.2	1.88	4.50	2.80

*BPNa for 0.95 NaPO₃, 0.05 Na₂B₄O₇ and BPCa for 0.9 Ca(PO₃)₂, 0.1 CaB₄O₇.

**theoretical concentrations (all other compositions have been checked)

TABLE 2 Second-Harmonic Generation Intensity recorded on glass samples poled at 300°C and 3kV

Glass sample	SHG signal (a.u.) at 800nm	SHG signal (a.u.) at 1.064 μ *
Fused vitreosil silica glass	100	100
BPCa matrix glass	1.5	25
BPCa-10.0%Nb ₂ O ₅	6	
BPCa-20.0%Nb ₂ O ₅	12	
BPCa-30.0%Nb ₂ O ₅	16	26

*The SHG response has been optimized by a cycling poling-depoling procedure¹²

FIG 1.a. Evolution of the experimental and calculated $\chi^{(3)}$ values for the titanium borophosphate glasses.

FIG 1.b. Evolution of the experimental and calculated $\chi^{(3)}$ values for the niobium borophosphate glasses.

Moreover, an interesting decrease of the signal under irradiation at 800nm has been characterized¹³. The creation of charge carriers inside the glass under irradiation, diffusing to the surfaces and neutralizing the charges accumulated under poling has been involved.

RAMAN, XAFS and XPS structural characterizations showed a progressively opening of the borophosphate network when introducing increasing proportions of niobium oxide, with the appearance of more non-bridging oxygen atoms. A comparable procedure is evidenced by XAFS and XPS on the anodic surface of a given composition when it is poled. After a thermal treatment during which the SHG is erased, the bridging bonds are restored¹². IR reflectance measurements show a slight but significant difference between poled and unpoled surfaces signals in the 960 to 1150cm⁻¹ region(FIGURE 2). The corresponding transitions are attributed to symmetrical and antisymmetrical vibration modes of terminal [PO₃⁻] groups on phosphate chains constituting the glass network. The decrease of the signal in this domain can be explained by an orientation of these groups perpendicularly to the anodic surface if the glass. On the basis of these results, the breakdown of isotropy induced by poling is evidenced. Whether such alterations can account for the measured SHG efficiency in niobium borophosphate glasses needs to be clarified. Ab-initio calculations under investigation could provide promising information.

FIGURE 2. Substraction of the IR reflectance signal of poled anode or cathode surface from the corresponding unpoled surface signal for the niobium borophosphate glass.

SUMMARY

This paper reviews nonlinear optical properties of sodium or calcium borophosphate glasses containing titanium or niobium oxides. The third order nonlinear efficiency is correlated to the concentration of d^0 ions in the glass. An enhancement is observed for the highest concentrations of titanium or niobium related to the clustering of TiO_n ($n = 5,6$) or NbO_6 entities. The second order nonlinear efficiency generated by thermal poling is observed in calcium borophosphate glasses and can be optimized by a cycling process. The nonlinear response is correlative to Na^+ impurities migration to the cathode during poling, opening of the glass network and reorientations of terminal $[PO_3^-]$ groups on phosphate chains near the surface in contact with the anode.

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