Conference materials
UDC 535.016
DOI: https://doi.org/10.18721/JPM.173.109

Ion exchange method for obtaining second-order nonlinearity in glass

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Abstract. In this work, we propose two-step process to create a second-order nonlinearity in glasses. First, we use the ion exchange method to form a region of an ion concentration and, consequently, conductivity gradient in glass. Afterwards, we apply DC voltage to the specimen at room temperature. This causes formation of non-equilibrium charge and inner electrostatic field, which induces effective second-order optical nonlinearity of the glass that exceeds one of thermally poled glass sample. After turning the voltage off, the effect gradually degrades within a few hundreds of seconds. Comparison of silver-for-sodium and potassium-for-sodium ion exchanges shows that in the latter case the result nonlinearity has longer relaxation time.

Keywords: glass, ion-exchange, Maxwell-Wagner effect, EFISH, second harmonic generation

Funding: The study was funded by the Ministry of Science and Higher Education of Russian Federation, project FSRM-2023-0009.

Citation: Kan G., Reshetov I.V., Terpitskiy A.N., Scherbak S.A., Lipovskii A.A., Ion exchange method for obtaining second-order nonlinearity in glass, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 17 (3.1) (2024) 47–51. DOI: https://doi.org/10.18721/JPM.173.109

Материалы конференции
УДК 535.016
DOI: https://doi.org/10.18721/JPM.173.109

Метод ионного обмена для получения нелинейности второго порядка в стекле

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Аннотация. Мы представляем двухэтапный процесс создания нелинейности второго порядка в стеклах. На первом этапе используется ионный обмен в стекле для формирования градиента концентрации подвижных ионов и, следовательно, градиента проводимости. На втором этапе прикладывается постоянное напряжение, наводящее неравновесный электрический заряд и внутреннее электростатическое поле, которое индуцирует в стекле эффективную оптическую нелинейность второго порядка, превышающую нелинейность термически поляризованного стекла. После отключения напряжения этот эффект постепенно затухает в течение нескольких сотен секунд. Сравнение ионного обмена серебро-натрий и калий-натрий показывает, что во втором случае время релаксации полученной нелинейности больше.

Ключевые слова: стекло, ионный обмен, эффект Максвелла-Вагнера, EFISH, генерация второй гармоники

Финансирование: Работа выполнена в рамках Государственного задания FSRM-2023-0009.

Ссылка при цитировании: Кан Г., Решетов И.В., Терпицкий А.Н., Щербак С.А., Липовский А.А. Метод ионного обмена для получения нелинейности второго порядка в стекле // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2024. Т. 17. № 3.1. С. 47–51. DOI: https://doi.org/10.18721/JPM.173.109

Introduction

It is well known that glass, due to its amorphous nature, is isotropic. However, modification of glass by thermal poling (TP) can break the isotropy in the near-surface layer [1]. The process involves heating a plate of glass, applying a constant voltage, and cooling under the voltage. Compositional analysis shows that the voltage forces mobile alkali ions of the glass to migrate from the sub-anode region. Differing in mobility hydrogen/hydronium ions from atmosphere compensate the deficit of electric charge in the depleted region. Therefore, regions with different conductivities are formed in glass. Current flow through them causes the accumulation of a non-equilibrium charge. That is known as the Maxwell-Wagner (M-W) effect [2]. Upon cooling, the charge "freezes" and forms an inner electrostatic field. The higher the dielectric constant of a material and the lower its conductivity, the longer the relaxation time of the non-equilibrium charge and electric field. This field mixed with the third-order optical nonlinearity of the glass leads to the appearance of an effective second-order nonlinearity (SON) and allows for second optical harmonic generation in glass, which is known as EFISH (Electric-Field Induced Second-Harmonic) effect [3].

We propose two-step process, alternative to TP, to create a second-order nonlinearity in glasses. At the first stage, we modify the glass by ion exchange (IE) [4] which allows creating a conductivity gradient where non-equilibrium charge accumulation is possible due to the M-W effect. In the second stage, we apply a DC voltage to the ion-exchanged samples. This results in electric charge accumulation and creating an effective SON.

Materials and Methods

For this study, we use a 1 mm thick soda-lime microscopic slide (Menzel) containing 14.3 wt.% of sodium oxide [5]. Potassium-to-sodium (K-Na) IE was carried out in a KNO_3 melt for 8 h at 365 °C, and silver-to-sodium (Ag-Na) IE – in a mixture of 5%/95% $AgNO_3/NaNO_3$ for 20 min at 325 °C. To confirm the presence of a concentration gradient in the samples, the potassium, silver and sodium concentration profiles across the sample were characterized using an Ultim Max 100 EDX spectroscopy (Oxford Instruments, UK) setup combined with a Supra 25 scanning electron microscope (Zeiss, Germany).

After, electric current flowing through the samples was characterized. In experiments, the samples were pressed between stainless steel electrodes, a DC voltage (1.3 kV) was applied and the current was measured using an A2-4 picoammeter (MNIPI, Belarus). A discharge of the accumulated electric charge was performed by short-circuiting the sides of the sample through the picoammeter. The charge/discharge of the samples were followed by the characterization of the second harmonic (SH) signal. The setup consisted of a Nano L ns-pulsed laser with an emission wavelength of 1.064 μm (Litron, UK), filters, a collecting lens and a photodetector. Also, we used ITO film electrodes transparent to the fundamental and second harmonic wavelength for simultaneous charge/discharge of the specimen and characterization of its SH signal. An incident angle of the radiation corresponded to the maximum of the SH signal from the sample. Note, preliminarily studies showed that ITO did not contribute to the SH signal. More details of the optical setup can be found elsewhere [6].

Results and Discussion

The concentration profiles of K-Na IE 8h-365 °C and Ag-Na IE 20min-325 °C samples obtained by EDX spectroscopy are shown in Figure 1, *a*, *b*, respectively. The profiles are ratiometrically normalized so that the sum of the ion concentrations equals to one. Figure 1 demonstrates that concentration gradients in the near-surface region have been formed. Depths of the profiles are ~6 and ~7 μm, respectively.

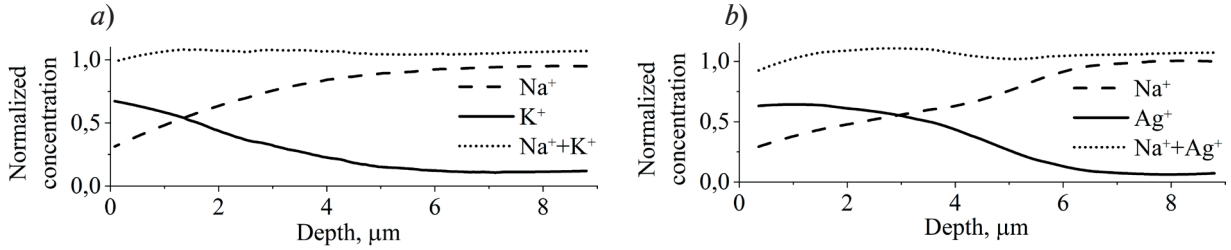

Fig. 1. Normalized concentration profiles of K-Na IE for 8 h-365 °C (*a*) and Ag-Na IE for 20 min-325 °C (*b*) measured by EDX spectroscopy

Then, the voltage was applied to the formed structures. The resulting graph of the current temporal dependence is demonstrated in Fig. 2, *a*. One can conclude that the presence of potassium gradient leads to the accumulation of non-equilibrium charge within 30 min. The Ag-Na IE sample charges much faster (~3 min). The same relates to the samples when discharging.

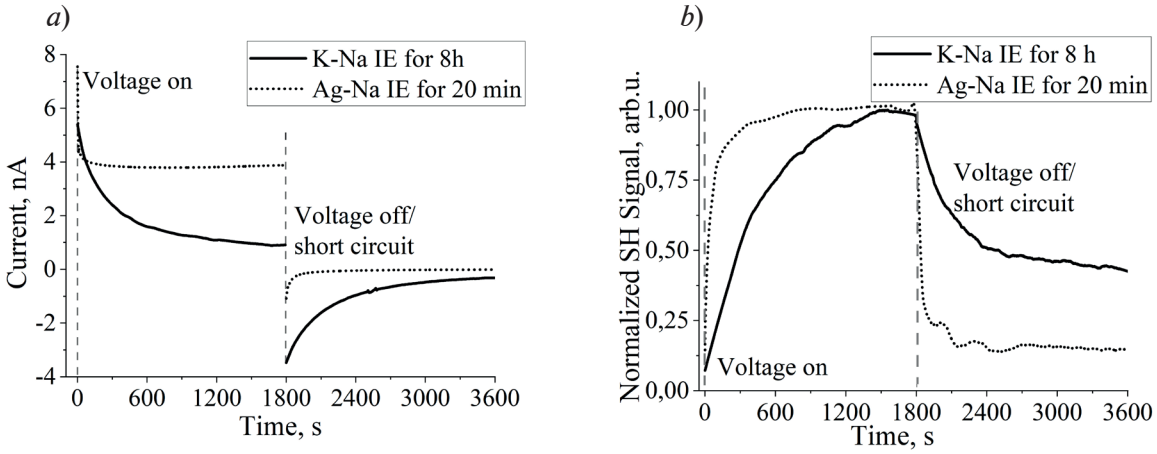

Fig. 2. Temporal dependences of the current (*a*) and normalized SH signal (*b*) with voltage on and off after 30 min

A similar estimation can be made from measuring the second harmonic dynamics (Fig. 2, *b*). The SH signal from Ag-Na IE sample saturates and relaxes much faster than one from the K-Na IE sample, and the characteristic discharge times correspond to those mentioned above. Besides, the discharge of K-Na IE sample takes longer than expected, and this needs further investigation.

This behavior can be explained by ionic mobility (see Table) and, respectively, the conductivity, which is inversely proportional to the relaxation time in the Maxwell-Wagner effect. Injection of less mobile potassium ions in glass leads to longer time of charge accumulation and dissolution, while more mobile silver ions fasten the processes.

Table

Mobility of ion species in soda-lime glass at T = 300 K

Ion species	Na^+	Ag^+	K^+
Mobility at T = 300 K, $m^2/(V \cdot s)$	$1.4 \cdot 10^{-20}$	$1.7 \cdot 10^{-21}$	$1.7 \cdot 10^{-22}$

The SH signal of the IE glasses can be compared with the one of thermally poled sample using Maker Fringe technique that is measuring SH intensity dependence on the incidence angle. For this purpose, K-Na IE glass sample was used, since Ag-Na IE one discharges faster than the measurement duration. Also, by restricting the access of the salt melt to one side, a single-side K-Na IE sample was obtained. TP was carried out using DC electric discharge in air gap [7]: DC voltage of 1.3 kV, temperature of 250 °C for 20 min. The result is shown in Fig. 3 for the single-side K-Na IE sample and the TP sample compared to the double side one. The SH intensity was normalized to the maximum of the SH value from the double-side sample.

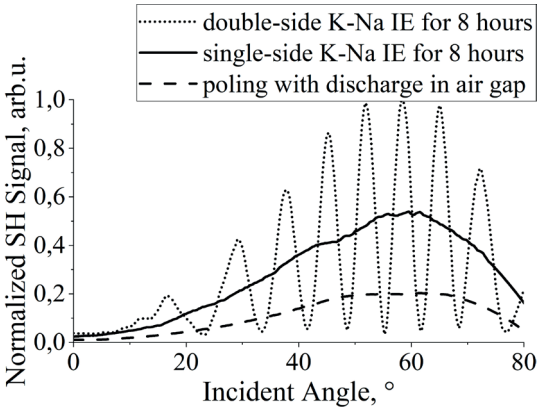

Fig. 3. Maker's Fringe pattern of double-side K-Na IE for 8h-365°C (dotted line), single-side K-Na IE for 8h-365°C (solid line) and sample poled using electric discharge in air gap (dashed line)

The fringes of dotted curve (double-side IE specimen) in Fig. 3 indicate interference between the SH signals from the two opposite sides of the glass slide. Two other curves (single-side IE and TP specimens) correspond to the signal generated only at one side. The single-side K-Na IE sample is given for direct comparison to TP. The SH intensity obtained from the single-side sample is ~2.5 times higher than that of the TP.

Conclusion

Thus, we demonstrate the formation of ion concentration and, consequently, conductivity gradient in glass after ion exchange that is sufficient for Maxwell-Wagner effect. This effect manifests in accumulation of electric charge and formation of inner electric field in the subsurface region of the glass upon DC voltage application. We registered it via measurements of optical second harmonic signal, which arises due to the EFISH effect. After turning the voltage off, the accumulated charge and corresponding electric field gradually dissolve within a few hundreds of seconds. We demonstrate that relaxation time varies depending on ion species used in IE.

Thus, ion exchange and subsequent room temperature voltage treatment is a new approach to induce and control optical nonlinearity of glasses that is comparable to one obtained by thermal poling.

Acknowledgments

The authors thank V.P. Kaasik for the assistance in the second harmonic measurements.

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Received 11.07.2024. Approved after reviewing 01.08.2024. Accepted 01.08.2024.