Inorganic clay-based nanostructured material for nonlinear optical waveguides

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\textbf{ABSTRACT}

A novel Laponite-lithium iodate nanocomposite has been synthesised for nonlinear optical applications. The elaboration starts with the addition of a lithium iodate aqueous solution to a colloidal suspension of Laponite JS. Thin layers, elaborated using dip-coating technique, form waveguides and the linear dependence between volume lithium iodate concentration and refractive index and the control of the thickness allow to optimise wave guiding properties. Waveguides show an attenuation of about 2 dB/cm and easily detectable second harmonic generation. A nonlinear effective coefficient of 1.6 pm/V has been measured. X-ray structural characterisations show that after drying and heat-treatments between 150 and 200\degree C, lithium iodate crystallises in the matrix with crystal size ranging from 20 to 50 nm. Thanks to the natural dipole moment of lithium iodate, nanocrystals orientation could be controlled using external electric field. Effects of orientation on nonlinear optical properties has been measured and compared with simulations based on a 1D multi-layers matrix model considering the nanocomposite as a stack of linear and nonlinear layers with fixed or random orientation. A good agreement is achieved between experiments and simulations.

\textbf{Keywords:} Nanocomposite, SHG, Laponite, Waveguide, LiIO\textsubscript{3}

\section{1. INTRODUCTION}

Many studies have been performed concerning the elaboration of non-linear optical materials for frequency conversion. In recent years, alternatives were explored in doping sol-gel layers with organic molecules.\textsuperscript{1} Other recent studies on materials for second harmonic generation (SHG) consist in inclusion of non centrosymmetric nanocrystals in an amorphous matrix. Conventional method for glass fabrication\textsuperscript{2–4} or sol-gel process\textsuperscript{5, 6} have been used to produce these nanostructured materials.

In this paper, we describe the elaboration of a low cost non-linear optical material obtained by doping Laponite with lithium iodate, a material known for its high non-linear coefficient.\textsuperscript{7} The interest of Laponite which is generally used to produce catalytic, anti-static and protective coating at a very low cost, has been recently demonstrated in integrated optics.\textsuperscript{8}

\section{2. EXPERIMENTAL SECTION}

\subsection{2.1. Chemistry}

The Laponite is a synthetic Clay with the following chemical formula:

\[ Si_8(Mg_{5.5}Li_{0.4})_2H_4O_{24}Na_{0.7} \]

The structure is composed of an octahedral layer where two sites out of three are occupied by a magnesium atom and one site out of three by a lithium atom, between two tetrahedral layers with silicium atoms on each site (Fig.1). Laponite can be modified by addition of dispersing agents. The Laponite has a layer structure which, in dispersion in water, is in the form of disc-shaped crystals of about 30 nm diameter and 1 nm thickness. For this study, we used \textquotedblright Laponite JS\textquotedblright which allows high Laponite concentrations in water (up to 18 wt.%). The colloidal solution can be used even after a long time storage.

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2.2. Sol elaboration and sample shaping

The precursor solution is prepared at room temperature by dispersing 3 wt.% of commercial Laponite JS in distilled water under strong agitation. A lithium iodate aqueous solution is then added to the clear colloidal suspension in order to get a LiIO$_3$/Laponite volume ratio ranging from 10 to 60 % in the dry material. After filtration of the solution (0.4 µm filter), films are deposited on glass substrates using dip coating technique. The thickness of a mono-layer, ranging from 200 nm to 3 µm, depends on the withdraw velocity and on the viscosity of the sol.

2.3. Crystallisation and electric field orientation of LiIO$_3$ nanocrystals

After a drying of few days at 100°C, the layer is annealed in the temperature range 150°C-210°C in order to cause nucleation of LiIO$_3$. Due to the natural strong dipole moment of LiIO$_3$, it is possible to orientate nanocrystals c-axis in the plane of the layers by applying a high voltage between two electrodes deposited on the edges of the substrate. C-axis orientation perpendicularly to the surface is achieved using Corona discharges.

2.4. Characterisation devices

The first observation of the optical quality of the films is performed on a ZEISS metallographic microscope. It is also used for polarised light microscopy. The structure and the morphology of the composite films are analysed using a Philips \(\theta - 2\theta\) X-ray diffractometer. The thickness, refractive index and attenuation of the waveguides are simultaneously measured with a prism coupling technique (m-lines) at an incident wavelength light \(\lambda = 0.5435\mu m\). Then nonlinear optical properties are determined by using a Maker fringes setup with a Q-switched Nd:Yag laser operating at \(\lambda = 1.064\mu m\) as fundamental wave.

3. STRUCTURAL CHARACTERISATION

XRD diagrams of pure Laponite layers are in good agreement with those observed on RD Laponite layers\(^8\) showing a large parallel orientation of Laponite particles on the substrate. During annealing, the water localised in the inter-particle spaces evaporates inducing particle aggregation and densification of the layer (Fig.2).

The lithium iodate solution is confined in these spaces and crystallises during annealing at temperatures ranging from 150 to 220°C. The structure of Laponite film naturally oriantates nanocrystals growth with the x-axis perpendicular to the plane of the layer as it can be seen on XRD pattern in Fig.3-a where (100) peak of \(\alpha\)-LiIO$_3$ is predominant. This is confirmed on polarised light microscopy image in Fig.3-b indicating that
nanocrystals grow from nucleation centre with c-axis in all directions of the layer plane, forming large self-organised domains (50-500 µm).

The orientation of nanocrystals has a strong impact on nonlinear optical properties. Indeed it allows to use the most efficient nonlinear coefficient or to carry out periodically oriented structures for quasi phase matching.

The nanocrystals are naturally oriented with the c-axis in the plane of the layer. Due to the strong electric dipole moment of LiIO$_3$ along the c-axis, it is possible to induce a preferential orientation by applying a high electric field (1 to 5 kV/cm) during annealing (ie during nucleation) between two electrodes deposited on the edges of the substrate (Fig.4a). This has been observed on a polarised light microscopy image in Fig.4b) where the domaines are largely deformed along the field lines. A schematic representation of nanocrystals organisation is given in Fig.4c)

4. LINEAR OPTICAL PROPERTIES

Nanocomposite thin layers deposited on glass substrates form planar waveguides. Refractive index of composite material depends on LiIO$_3$ concentration as shown in Fig.5-a. Experimental points are in good agreement with the predictions of Maxwell-Garnett theory describing the linear optical properties of composite materials. Due to the low difference between laponite and LiIO$_3$ dielectric permittivities, this relation can be considered as linear.

The control of the thickness and of the refractive index allows waveguides elaboration. The image in Fig.5-b shows the light diffused at the surface of a waveguide. An attenuation of 2 dB/cm has been measured for a nanocomposite waveguide doped with 25 Vol.% of LiIO$_3$.

5. NONLINEAR OPTICAL PROPERTIES

5.1. Nonlinear effective coefficient measurement

The effective nonlinear coefficient $d_{eff}$ is the main parameter to estimate the frequency conversion efficiency of a material. However its measurement, by comparison of the SH intensity generated by the composite sample with
Figure 4. Gold electrodes deposited on the edges of the layer a), polarised light microscope image showing consequences of an electric field in the plane of the layer b) and schematic representation of nanocrystals orientation in the domains c).

Figure 5. Refractive index versus LiIO₃ concentration compared with predictions of Maxwell Garnett theory a) and an image of diffused light at the surface of a waveguide b).

those of a x-cut quartz plate reference, requires to know the nature of the optical interactions at the origin of the second harmonic generation. Indeed, if there is no coherence, the total SHG can be seen as the sum of the individual contributions of each nanocrystal. This case is similar to the second harmonic generation in powder and the SH intensity is proportional to the length $L$ of crossed matter:

$$I_{2\omega} \propto d_{eff} I_{\omega}^2 L$$

(1)

On the other hand, coherence between the different contributions induces a quadratic relation between the intensity and the length of crossed material:

$$I_{2\omega} \propto d_{eff} I_{\omega}^2 L^2$$

(2)

The SH harmonic intensity versus the thickness of the layer has been plotted in figure 6.

Neither a quadratic nor a linear relation can be clearly determined by this experiment, but according to structural considerations we can make the assumption that the orientation is homogeneous along the propagation way so that the SHG can be seen as coherent.

With this consideration, a $d_{eff}$ coefficient of 1.6 pm/V has been measured on a composite sample doped with 50 Vol.% of LiIO₃.¹¹,¹²
The effective nonlinear coefficient is the most important parameter to quantify the nonlinear optical properties of a material. However, to understand the origin and the mechanisms of second harmonic generation in complex material, it is necessary to compare this experimental value to predictions of analytical or numerical models based on structural considerations.

5.2. Analytical calculation of the effective nonlinear coefficient

The nonlinear effective coefficient cannot generally be analytically determined for a composite material. However, it can be estimated, in the case of a volume proportion \( p \) of spherical inclusions (a) (in our case LiIO\(_3\)) in a matrix (b),\(^{13}\) by using the relation:

\[
d_{\text{eff}} = pd_{\text{eff}}^{(a)} \left( \frac{3\epsilon_b^b}{\epsilon_2^b + 2\epsilon_b^b} \right) \left( \frac{3\epsilon_b^a}{\epsilon_2^a + 2\epsilon_b^a} \right)^2
\]

where \( d_{\text{eff}}^{(a)} = 6.2\) pm/V is the LiIO\(_3\) mean nonlinear effective coefficient (in the case of a composite were all nanocrystals have c axis in the plane of the layer as observed in the structural description §3) given by the integral:

\[
<d_{\text{eff}}^{(a)}> = \frac{1}{2\pi} \int_0^{2\pi} d_{\text{eff}}^{(a)}(\theta), d\theta
\]

where \( d_{\text{eff}}^{(a)}(\theta) \) is the effective nonlinear coefficient in the direction of polarisation \( \theta \):

\[
d_{\text{eff}}^{(a)}(\theta) = \sqrt{2(2d_{15}^2 + d_{13}^2)d_{33}^a \sin(\theta)^2 \cos(\theta)^2 + d_{13}^2 \sin(\theta)^4 + d_{33}^a \cos(\theta)^4}
\]

The equation 3 leads to a coefficient value \( d_{\text{eff}} = 2.2\) pm/V which is close to the experimental value. This model takes into account the nonlinear properties of the inclusions and the local electric field enhancement due to the refractive index (ie dielectric permittivity) difference between the nanocrystals and the matrix.

A simpler model, consists in considering the material as a stack of alternative linear and non-linear layers.\(^{14,15}\) With an incident light polarisation in the plane of the layer (s), the continuity of the tangential component of the electric field leads to the simple expression for the nonlinear effective coefficient:

\[
d_{\text{eff}} = pd_{\text{eff}}^{(a)}
\]

For a composite with 50% vol. of LiIO\(_3\) we find then \( d_{\text{eff}} = 3.1\) pm/V. If this value over-estimates the experimental value, this model, in adequacy with the structural considerations, seems well adapted to the description of the composite.
If these analytical models are efficient to estimate the non-linear effective coefficient, they are not adapted to describe complex structure presenting random dispersions on nanocrystals size and orientation. That’s why a matrix model has been developed to simulate the SHG of any structure.

5.3. Matrix model

A matrix model has been elaborated from theoretical studies to evaluate the influence of parameters such as LiIO$_3$ concentration, nanocrystals size and orientation on non-linear response. In this model, we consider the composite material as a stack of alternative linear and non-linear layers so that it is possible to study complex structures. As an example, simulations of second harmonic intensity for different nanocrystals orientations and volume ratio in the nanocomposite are compared to SHG of a LiIO$_3$ x-cut single crystal in Fig. 7-a.

![Diagram showing analytical model and simulations](image)

Figure 7. Modelisation of second harmonic intensity as a function of LiIO$_3$ vol. concentration for a) naturally oriented (experimental case), b) x oriented and c) randomly oriented nanocomposites. The SHG levels of a bulk x-cut LiIO$_3$ crystal and of the analytical model described in eq. 6 are reported.

First of all, the good agreement between analytical and matrix models for nanocomposites oriented with c-axis nanocrystals in the plane of the layer validate there use to predict SHG in the nanocomposite material.

Then, we can see that the SH intensity of the naturally oriented nanocomposite doped with 50% vol. of LiIO$_3$ (experimental case) is only 5 times lower than that of an x-cut LiIO$_3$ single crystal.

Finally, we observe a large difference (2 orders of magnitude) between the SH intensities generated by an oriented structure and those of a randomly oriented nanocomposite. This can be explained by the coherence between each nanocrystal SH contribution. As we already mentioned, this coherence, provided by a constant orientation of nanocrystals along the propagation direction, increases the output SH signal. Total SH intensity
is then proportional to $L^2$. In the case of a randomly oriented material, no coherence is observed and the total SH intensity is the sum of each nanocrystal contribution as in the case of a powder ($I_{2\omega} \propto L$).

Regarding these results, it appears necessary to orientate the nanocrystals to obtain an efficient frequency conversion.

6. CONCLUSION

A new inorganic clay-based nanocomposite has been synthesised for waveguided second harmonic generation. Structural study has shown that during annealing, LiIO$_3$ nanocrystals grow as self organised large domains with the c-axis in the plane of the layer. Optical characterisations have shown a linear dependence between refractive indexes and LiIO$_3$ amount in the composite. The waveguides attenuation measured at about 2 dB/cm is large but could be decreased by the optimisation of chemical preparation and deposition process. A value of 1.6 pm/V has been measured for the effective non-linear coefficient. This high value for an inorganic compound, associated with the control of nanocrystal c-axis orientation could offer the possibility to enhance frequency conversion efficiency by carrying out periodic structures for quasi phase matching.

REFERENCES