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Optical characterization of PZT thin films for waveguide applications

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Abstract

In order to develop an electro-optic waveguide, Pb(Zr, Ti)O_3 ceramic ferroelectric thin films were elaborated by a modified sol–gel process on glass substrate. In the aim to study the optical properties of the PZT films, an accurate refractive index and thickness measurement apparatus was set up, which is called M-lines device. An evaluation of experimental uncertainty and calculation of the precision of the refractive index and thickness were developed on PZT layers. Two different processes of PZT elaboration were made and studied with this apparatus. The reproducibility of one fabrication process was tested and results are presented in this paper.

Keywords: Sol–gel processes; Optical properties; PZT; Waveguide

1. Introduction

In integrated optics, various applications are based on the utilization of thin film planar waveguides. The approach to use PZT transparent ceramic films for the realization of such waveguide structures will be reported in the present paper. The PZT thin films were elaborated by a chemical solution deposition (CSD) technique and were spin-coated on glass substrates. The main characteristic parameters for the realization of a planar waveguide are the refractive indexes and the thicknesses of the different layers constituting the waveguide.[1] In order to accurately measure these parameters, a prism-film coupler device was used (so-called M-lines technique) at the 632.8 nm He–Ne laser wavelength allowing to determine the phase matching angles (coupling modes). Numerical resolution of the planar waveguide equation allows to relate these angles to the mode order, to the refractive index, and the film thickness. Evaluation of different uncertainty of our experimental set-up and a differential calculus allows to quantify the accuracy of the refractive index and the film thickness.

2. Film deposition and characterization

$Pb_{1.4}Zr_{0.36}Ti_{0.64}O_3$ thin films were elaborated by a (modified sol–gel process) chemical solution deposition technique and spin-coated on glass substrates (Corning 1737f). The precursor solution consisted of lead acetate dissolved in acetic acid, zirconium and titanium *n*-propoxide; ethylene glycol was added in order to prevent from crack formation during the annealing process. The deposited films were dried on a hot plate and a rapid thermal annealing (RTA) procedure at 620 °C resulted in the formation of a polycrystalline perovskite phase.[2,3] The substrate has been selected because of its thermal expansion coefficient close to this of bulk Pb(Zr, Ti)O_3. This minimizes thermal strains in the film during the heating process, reduces the number of cracks and consequently increases the optical quality of the thin films. The structure of the films was characterized by SEM and X-ray diffraction and their optical properties were investigated with M-lines spectroscopy.[4] We will focus on this optical characterization because the refractive index is one of the major parameters for the design of waveguides. A classical M-lines device was set up in the configuration shown in Fig. 1. The light of a He–Ne laser is focused to the base of a prism, which is pressed against the film. The prism and the film are mounted on a rotating stage allowing to vary the angle of incidence. The incident light is totally reflected by the interface

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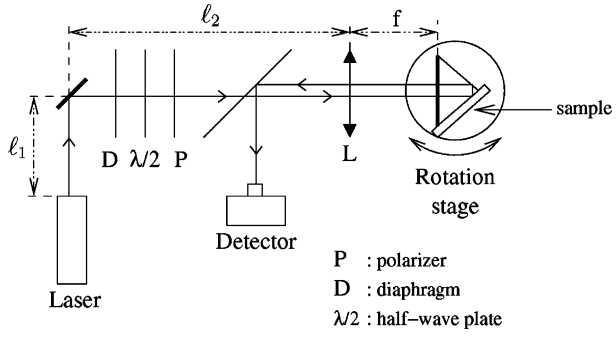

Fig. 1. M-lines experimental set-up: $l_1 = 13$ cm, $l_2 = 59$ cm and $f = 20$ cm.

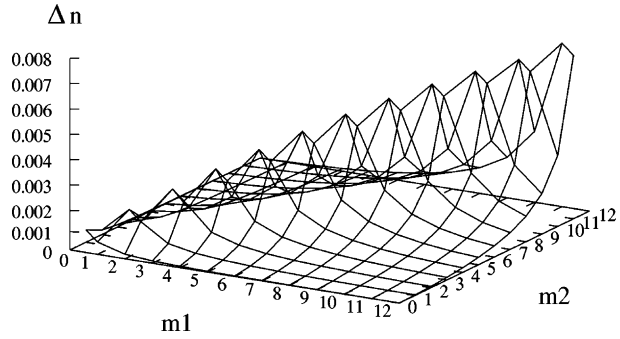

Fig. 2. Index uncertainty as a function of the two mode orders.

prism-film for all angles except synchronous angles where it is coupled into the film. For TE modes, these synchronous angles are given by the dispersion equation of planar waveguides:

$$m\pi = d\,k_0\sqrt{n^2 - N_m^2} - \text{arctg}\left(\sqrt{\frac{N_m^2 - n_\text{a}^2}{n^2 - N_m^2}}\right) - \text{arctg}\left(\sqrt{\frac{N_m^2 - n_\text{s}^2}{n^2 - N_m^2}}\right) \quad (1)$$

where m is the order of the guided mode, d is the thickness of the film, n, n_a, n_s are, respectively, the film, the air and the substrate refractive index and N_m is the effective index of the guided mode. N_m depends on the synchronous angles ϕ_m:

$$N_m = n_\text{p}\sin\left[A_\text{p} + \arcsin\left(\frac{\sin\phi_m}{n_\text{p}}\right)\right] \quad (2)$$

where A_p is the angle of the prism and n_p is its refractive index. In the dispersion Eq. (1), the two parameters n and d are unknown. Hence, it is necessary to measure at least two modes in order to determine them.[5]

The precision of the method is determined by the precision of the angle measurement. The rotation is done by a step by step motor having a step size of 0.001°, which can be considered as the maximum precision. In the real experiment, other uncertainties lower than this precision, the most important of which is the uncertainty on the position of the zero angle. Experimentally, this position was defined by superimposing the backward and forward beams on the diaphragm (see Fig. 1). In order to evaluate numerically this uncertainty, we suppose that the beams are superimposed if their centers are closer than one radius. With the focal length of the lens L of 20 cm and a beam waist of the laser of 400 μm, an uncertainty of the zero angle position of 0.05° is found.

The influence of this error on the values of n and d is calculated with the help of a set of two dispersion Eq. (1) for two modes m_1 and m_2. By differentiating these equations, we obtain the uncertainty on n and d as a function of the uncertainties of the other parameters: $\Delta n = G_n(\Delta n_\text{a}, \Delta n_\text{s}, \Delta N_{m_1}, \Delta N_{m_2})$ and $\Delta d = G_d(\Delta n_\text{a}, \Delta n_\text{s}, \Delta N_{m_1}, \Delta N_{m_2})$ where ΔN_{mi} depends on ΔA_p, Δn_p and $\Delta\phi_{mi}$.

The Fig. 2 shows the uncertainty of refractive index as a function of the mode orders for a 2.08 μm thick film having an index of 2.427 (the M-lines spectrum is represented in Fig. 3) for angle uncertainties of 0.05°. The uncertainty of the refractive index increases with the mode orders, however, remains smaller than $\pm 8 \times 10^{-3}$.

3. Mode indexing

Usually, mode indexing is not a very difficult task. Under certain circumstances, however, especially when developing a film processing method, great care must be taken since the validity of the dispersion equation is restricted to homogeneous, isotropic and lossless guides. Films that deviate from these ideal conditions could give erroneous results. The criterion usually used for indexing states that the first appearing mode is the zero order mode. In the case of real films, however, it is sometimes very difficult to excite this fundamental mode because of the large angle of incidence. The peak corresponding to the zero order mode is then missing in the M-lines spectrum. This is illustrated in the Fig. 3, which shows the M-lines spectrum of a $Pb_{1.4}Zr_{0.36}Ti_{0.64}O_3$ thin film crystallized in the pyrochlore phase. In our set-up, the fundamental mode appears at high angles. A tiny peak around 37° can be seen which is hardly measurable and appeared to be insensitive to

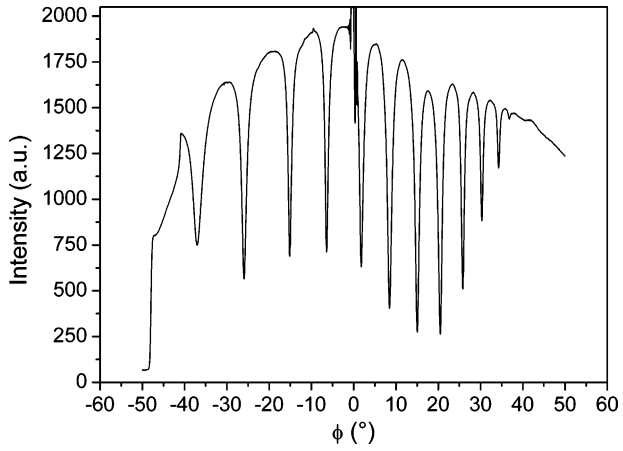

Fig. 3. M-lines spectrum of a 2.08 μm thick pyrochlore film.

the pressure applied to the film. Thus, it is not certain that this peak is the fundamental mode. In order to overcome the mode order indexation difficulty, we suggest the following procedure. For a spectrum consisting of M modes, we suppose that the first mode is equal to zero, the second to one and so on. Using the Eq. (1), we calculate the C_M^2 couples (n, d) of solutions corresponding to the different combinations of two modes. With this couples (n, d) of solutions, using the same equation, M synchronous angles ϕ^{calc} are obtained. Then we build the σ_m function (Eq. (3)) which is the square root of sums of each mode and of each combination of the quadratic difference between these ϕ^{calc} and the measured synchronous angles ϕ^{meas}:

$$\sigma_m = \sqrt{\sum_{i=1}^{C_M^2} \sum_{j=1}^{M} \frac{(\phi_{ij}^{\text{calc}} - \phi_{ij}^{\text{meas}})^2}{MC_M^2}} \tag{3}$$

This calculus is repeated several times while incrementing each mode by one unit, i.e. in the second step, the first mode is equal to one ($m = 1$), the second is equal to two and so on. Applying this procedure in order to analyze the spectrum of Fig. 2, we find a σ_m as a function of the first mode order as shown in Fig. 3. Numerical simulations showed that the smallest σ_m results in a correct indexing for angles measurement errors smaller than 0.5°. On Fig. 4, the minimum appears for $m = 1$, thus the first peak of the spectrum (around 37°) is not the fundamental mode.

Once the indexing is finished, an optimization method is necessary in order to find the actual refractive index and the thickness of the film because of the dispersion of values resulting from the different mode combinations. The simplest method is to calculate mean values; however, for a number greater than four, we prefer to use a simplex algorithm which allows to reduce systematic errors of the origin of the angles.[6] In the case of the studied film, this optimization gives the following results: $n = 2.427 \pm 2 \times 10^{-3}$ and $d = 2.08 \pm 2 \times 10^{-2}$ μm.

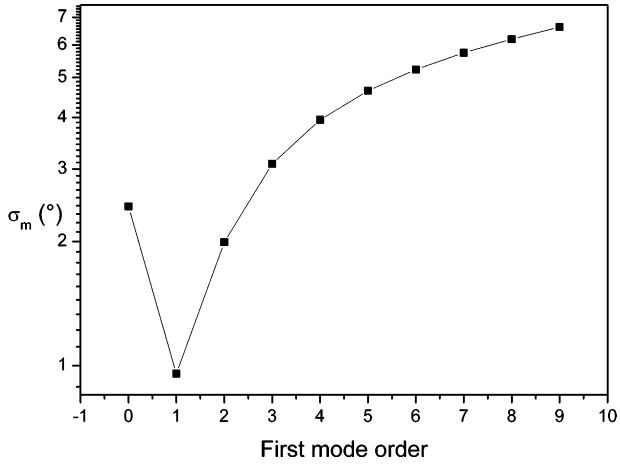

Fig. 4. The σ_m curve as a function of the first mode order.

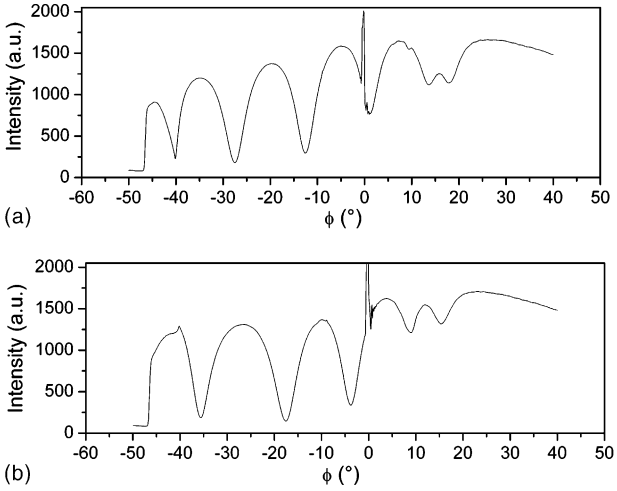

Fig. 5. M-lines spectrum on two PZT sample elaborated with both methods: (a) cooling outside the oven; (b) cooling inside the oven.

4. Study of ferroelectric films

Convenable waveguides are realized from homogeneous films of the order of 1 μm thickness. The difficulty which arises for this type of layers is that cracks may appear during the crystallization process. In order to limit these cracks, we compared two cooling methods after the heat treatment, one outside the oven and one inside the oven. No apparent differences were visible from a macroscopic point of view.

The M-lines spectra obtained for the two methods are represented in Fig. 5. Despite of only a modification in the heat treatment, the M-lines spectra show considerable differences in the position of the individual peaks. A series of six identical samples was prepared for each cooling procedure, the M-lines spectra were acquired, and the above described indexing method was applied. Sums σ_m for cooling outside and inside the oven are given in Fig. 6a and b, respectively, showing a qualitative difference of the two series.

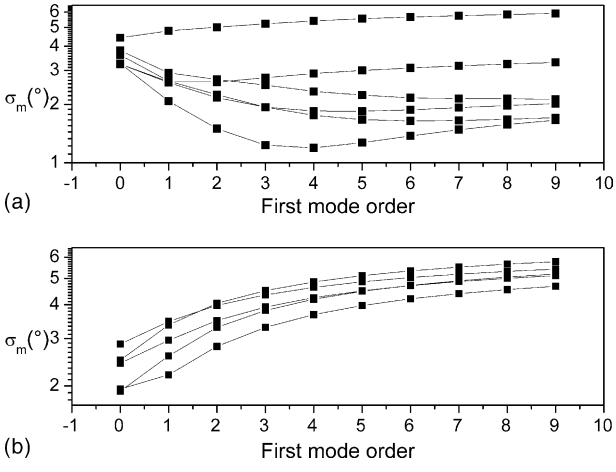

Fig. 6. σ_m curves as a function of the first mode order for: (a) cooling outside the oven; (b) cooling inside the oven.

Table 1
Mean values and dispersion of the refractive index and the film thickness of the two series S_1 and S_2

Series	$\langle n \rangle$	Max $\lvert n - \langle n \rangle \rvert$
S_1	2.224	6×10^{-3}
S_2	2.221	7×10^{-3}
	$\langle d \rangle$ (μm)	max $\lvert d - \langle d \rangle \rvert$
S_1	0.92	1×10^{-2}
S_2	0.87	3×10^{-2}

For the films having undergone a cooling outside the oven, it is either impossible to find a minimum, or the indexing obtained leads to absurd values of n and d. Apparently, the thermal shock imposed to the samples while retrieving them from the oven, results in a modification of the films, which is macroscopically invisible. However, it can be detected by M-lines spectroscopy. While no direct evidence on the structural properties of the films may be derived from these measurements, the results show non-conformities between the experimental data and the modelization used to establish the dispersion equation of the planar waveguide. Thus, we conclude that this elaboration method is not adapted to realize a step-index waveguide. The films having undergone a slow cooling inside the oven (Fig. 6b) present a minimum for $m = 0$, which corresponds to a refractive index close to 2.22 and a thickness of approximately 0.87 μm. In the case of this heat treatment, the films realized correspond well to the step-index waveguide model.

The homogeneity of the films and the reproducibility of the elaboration method have been studied with M-lines spectroscopy, too. Two series (S_1 and S_2) of six films, elaborated under the same conditions (composition of the solution, parameters of spin-coating, temperature and duration of the heat treatment, etc.), have been investigated. In the case of these films, the synchronous angles could be determined with a precision of only 0.1° due to rather flat peaks in the M-lines spectrum. Using the error calculation described in the previous section, we find an uncertainty of $\pm 3 \times 10^{-3}$ for the refractive index and $\pm 8 \times 10^{-3}$ μm for the film thickness.

In order to determine the lower limit of the measurement accuracy of our experimental set-up, the films were measured many times at the same point. The maximum difference of refractive index and thickness for all measurement are, respectively 2.2×10^{-3} and 5×10^{-3} μm. These values are consistent with the uncertainties previously calculated. The mean values and the dispersion of the refractive index and the thickness of the two series of samples are presented in Table 1. One can see that the values are almost identical for both series, and the differences are smaller than the dispersion within one series. From this overlapping of results between the two series, we deduce a reproducibility of the elaboration process, of the order of 5×10^{-3} for the refractive index and 20 nm for the thickness of the films.

5. Conclusions

In the present paper, a consistent method for indexing the peaks of M-lines spectrum obtained from PZT thin films was proposed. We have shown that the classical indexing criterion sometimes fails, and we proposed a method to test the consistency of the spectra. This method provides good results and can be applied to films, which are not too far from the ideal step-index waveguide. By successively measuring identical points of a sample, the sensibility of the M-lines set-up could be determined. The reproducibility of the elaboration process was quantified. In a preliminary study of the optical properties of spin-coated PZT thin films, we have shown the crucial influence of the heat treatment procedure. The proposed method will also allow the study of other elaboration parameters.

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