STRUCTURE EFFECTS ON THE OPTICAL PROPERTIES OF THIN (PbLa)TiO₃ FILMS

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Abstract — Amorphous thin films of Pb₁₋ₓLaₓTiO₃ (with x=0, 13 and 27 mol %) were prepared by the polymeric precursor method and deposited by spin coating on glass substrates. The films were characterized by X-ray diffraction (XDR) and scanning electron microscopy (SEM) and the band gap energy of the amorphous PLT films was calculated from the UV-VIS spectra. The obtained values were compared to that theoretically calculated. The observed decrease of the band gap was attributed to increased density of defects in the amorphous structure. Furthermore photoluminescence (PL) at room temperature was observed for thin (PbLa)TiO₃ films.

Keywords — thin films, optical properties, amorphous, titanate and photoluminescence.

I. INTRODUCTION

Preparation of thin films by deposition of a chemical solution is a promising process for the fabrication of optoelectronic devices (Ridley et al., 1999). Chemical solution deposition offers a wide variety of applications, including ferroelectric thin films, high-density optical data storage or semiconductors (Pontes et al., 2000a; and Maeda et al., 1993). In addition, the chemical solution process allows to prepare amorphous compounds that cannot be prepared by the usual melting processes.

Pizani et al. (2000) and Leite et al. (2000a) reported intense room temperature PL for amorphous PbTiO₃ (a-PT) powders and thin films deposited on Si (100). In these studies, a simple chemical method was used to process powders and thin films at low temperatures (T < 400 °C). The PL observed in a-PT showed a strict relationship with disorder in the perovskite structure. Study of the a-PT structure by X-ray absorption near edge structure (XANES) showed that these compounds are basically formed by six-fold oxygen-Ti coordination (TiO₆-octahedra) and fivefold oxygen-Ti coordination (TiO₅-square-base pyramid) as it is reported by Pontes et al. (2000b).

Firstly, a simple water-based chemical process was used, allowing amorphous titanates to be processed at temperatures as low as 250°C in the form of thin films or particles. Secondly, theoretical and experimental results suggest that amorphous titanate is composed of a Ti-O network.

Recently our group demonstrated that amorphous titanates (ATiO₃, with A=Pb, Ca, Sr and Ba), processed by a soft chemical process called the polymeric precursor method, displayed intense PL at room temperature (Pizani et al., 2000; and Leite et al., 2000a).

Optical properties like PL are not usually observed, but due to their interesting PL properties, amorphous materials of the ATiO₃ type, such as Pb(Zr,Ti)O₃ (PZT), BaTiO₃ (BT) and SrTiO₃ (ST) have been the target of several studies (Leite et al., 2000a; Pontes et al., 2000b; and Leite et al., 2000b).

Investigations of the optical absorption edge give information on the band structure of a material and its changes, which are especially important for crystals showing ferroelectric phase transitions (Yakubovs et al., 1974).

The absorption edge of amorphous semiconductors is structure sensitive, on the other hand, the purity and method of preparation directly influence the optical absorption, particularly in the case of thin films (Wood and Tauc, 1972).

The absorption spectra of amorphous semiconductors at different photon energies suggest three different parts. Two of them are similar in different materials and are easily reproducible. The third part (absorption edge) is a structure-sensitive and a characteristic of amorphous semiconductors (Wood and Tauc, 1972).

This report presents the preparation of thin amorphous PLT films and studies their band gap energy calculated from UV-VIS spectra and compared to that determined by theoretical calculations. The PL intensity is also presented as a function of the Pb cation substitution by La in the pure PbTiO₃ lattice.

II. METHODS

Pb₁₋ₓLaₓTiO₃ thin films, in which x is the amount of La that substitutes Pb (x = 0, 13 and 27 in mol%) were prepared by the polymeric precursor method, as it is schematized in Fig. 1. The polymeric precursor method (Le-