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Luminescence effect in amorphous PLT

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Abstract

Amorphous and crystalline powder of PLT phase was synthesized by using the Pechini method. Infrared (FTIR) analysis of the polymeric resin shows intense bands of organic materials from 250 to 1620 cm^{-1}. X-ray diffraction (XRD) and Raman spectra of calcined powder at different temperatures show amorphous phase at 450 °C/3 h, semi-crystalline phase at 550 °C/3 h and a crystalline phase at 800 °C/3 h. Luminescence effect was observed in amorphous powder calcined from 300 to 350 °/3 h with broad absorption peaks in 579 nm at 300 °C/3 h and 603 nm at 350 °C/3 h, respectively. The photoluminescence effect is attributed to emissions of Ti → O directly from the oxygen 2p orbital (valence band) to the titanate 3d orbital (conduction bands).

Keywords: Amorphous materials; Perovskites; PLT; (Pb, La)TiO_3; Luminescence

1. Introduction

Great interest has been shown in the study of the active optical properties, such as photoluminescence (PL) or non-linear optics of amorphous materials at room temperature, of special interest have been the perovskite type titanates. Lead lanthanum titanate (PLT), lead lanthanum zirconium titanate (PLZT), and lead zirconium titanate (PZT) have received considerable attention in view of potential applications such as ferroelectric random access memories,[1] pyroelectric IR sensors[2] optical total internal reflection switches,[3] spatial light modulator,[4] surface acoustic wave devices and piezoelectric sensors.[5]

Crystalline $PbTiO_3$ (PT) has a tetragonal ABO_3-type structure. Studies of the optical characteristics of PT indicate that the emission of photons is related to $Ti^{3+} \rightarrow O^{2-}$ charge transfer in the $[BO_{6-\delta}]$ octahedra.

Investigations by Meng et al.[6] have shown that systems based on crystalline $Ba_{1-x}Pb_xTiO_3$ and $Sr_{1-x}Pb_xTiO_3$ present photoluminescence at room temperature. It was observed that the effect depends on the surface state distribution and on the associated electronic structure. Leonelli and Brehner[7] have put forward a model to explain the mechanism of visible emission in which the electrons form small polarons, while the holes interact with the polarons to form self-trapped excitons (STEs).

Pizani et al.[8] recently reported efficient room temperature photoluminescence (PL) in both amorphous $PbTiO_3$ powder and in thin films prepared on silicon wafers. Rangel et al.[9] studied visible photoluminescence (PL) properties changing with surface morphology and with the structure in amorphous α-$PbTiO_3$ thin films processed by a polymeric precursor method.

Additions of lanthanum to PT improve the mechanical and ferroelectric characteristics of the material. Sei et al.[10] studied the refractive index of PLT prepared by sol–gel route and found that it increased with increasing crystal size of the PLT. Lanthanum in crystalline PT does not lead to photoluminescence effect. However it is know well that 9 mol% of La caused electro-optic effect in PZT. Thus the purpose of this work is to conduct the synthesis of amorphous $PbLa_{0.09}(TiO_3)$ and to study the photoluminescence characteristics. The synthesis used is the polymeric precursor method developed by Pechini.[11]

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2. Experimental procedure

The composition of the investigated material was $PbLa_{0.09}(TiO_3)$. For the synthesis of this material titanium isopropoxide, lead nitrate and lanthanum oxide were used as raw materials (Table 1).

A polyester resin was prepared based on a mixture of 0.35 mol% of titanium isopropoxide and 50 g of citric acid with ethylene glycol at 60/40 molar ratio. Lead oxalate (0.91 mol%) was precipitated into the resin and stirred until a clear sol formed. A solution of lanthanum oxide (0.09 mol%) dispersed in acid medium was added to resin at 120 °C. After polyesterification at 140 °C those resin was finally calcined from 200 to 500 °C.

The resin was analyzed by infrared (IR) (Shimadzu model FT-IR 4200). Differential thermal analysis (DTA) was carried out (Netszch, STA 409) in synthetic air with flow rate of 20 cm^3/min up to 1200 °C with a heating rate of 5 °C/min.

2.1. X-ray diffraction pattern

The amorphous and crystalline character of the material was assessed by means of X-ray diffraction (XRD) pattern by using a SIEMENS model D 5000. The Cu Kα radiation with λ of 1.5418 Å and with a range of angles from $2\theta = 10°$ to 80° and steps of 0.05 was used.

2.2. Luminescence analyses

A U1000 Jobin–Yvon double monochromator coupled to a cooled GaAs photo multiplier and conventional photon counting system was used to obtain the photoluminescence spectra. The 488 nm exciting wavelength of an argon ion laser was used. The maximum output of the laser was 500 mW and a cylindrical lens was provided to prevent the sample overheating. The slit used was 250 μm; all measurements were taken at room temperature.

Table 1
Raw material used in the PLT synthesis

Material	Origin	Percent
Titanium isopropoxide	Aldrich	99.00
Lead acetate	Carlo Erba	99.50
Lanthanum oxide	Aldrich	99.99
Ethylene glycol	E. Merck	99.50
Citric acid	E. Merck	99.50

3. Results and discussion

3.1. Phase analysis

Fig. 1 shows the infrared (FTIR) analyses of the PLT polymeric precursors polymerized at 260 °C. Intense bands of organic material was observed from 250 to 4000 cm^{-1}. For the polymeric precursor polymerized at 260 °C vibrations at 1620 cm^{-1} were observed, related to the C=O stretching mode for ester groups (R–COO–R). During polymerization a chain of Ti citrates is formed caused by ethylene glycol addition.

Fig. 2 shows the XRD pattern of resin decomposition at 450 °C with a broad peak at $2\theta = 28°$ indicating nucleation of the PLT phase. A diffuse semi-crystalline phase presence was observed and at this temperature there is still a large

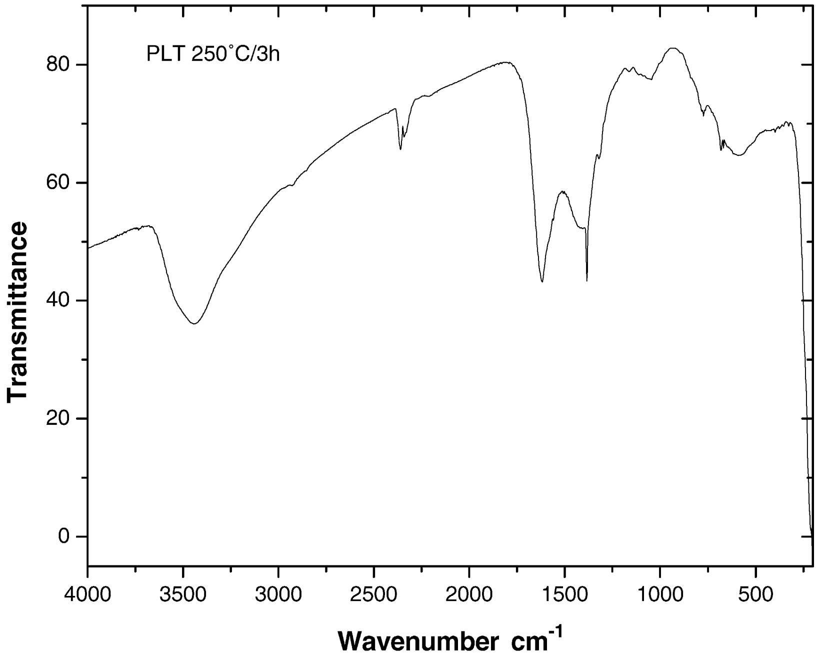

Fig. 1. Infrared (IR) analysis of polymeric resin of the PLT.

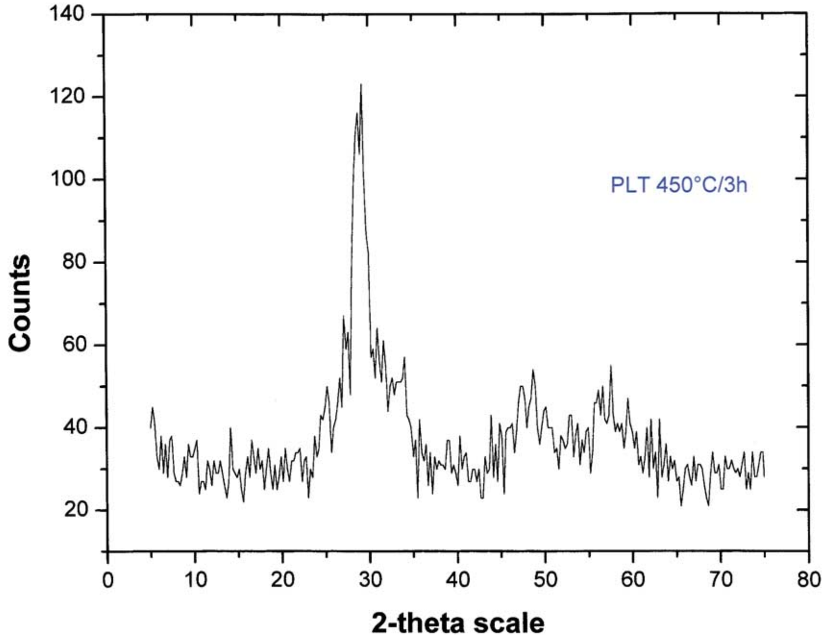

Fig. 2. X-ray diffraction pattern of powder calcined at 450 °C/3 h.

amount of organic material. Analysis by X-ray diffraction pattern at 700° C/3 h, Fig. 3 shows that a non-homogeneous tetragonal PLT phase was obtained with intense crystalline peaks. There were also peaks of PbO phase at $2\theta = 28.5°$ and $2\theta = 31.8°$ relative to an excess of PbO during calcinations.

Observations by Raman, at 450, 550, and 800 °C, Fig. 4 shows the presence of a large amount of amorphous phase at 450 °C due to a incidence of small peaks of the crystalline phase. This is observed by XRD at 450 °C. Fig. 2 shows non-defined peaks of the PLT phase. The Raman spectra from 550 to 800 °C show an increase of peaks of the crystalline phase.

3.2. Luminescence effect

Fig. 5 shows an analysis of photoluminescence in the visible region of amorphous and semi-crystalline powder. From 250 to 450 °C an intense peak of photoluminescence is observed at 250 and 300 °C (amorphous powder). The photoluminescence effect does not occur for the composition at

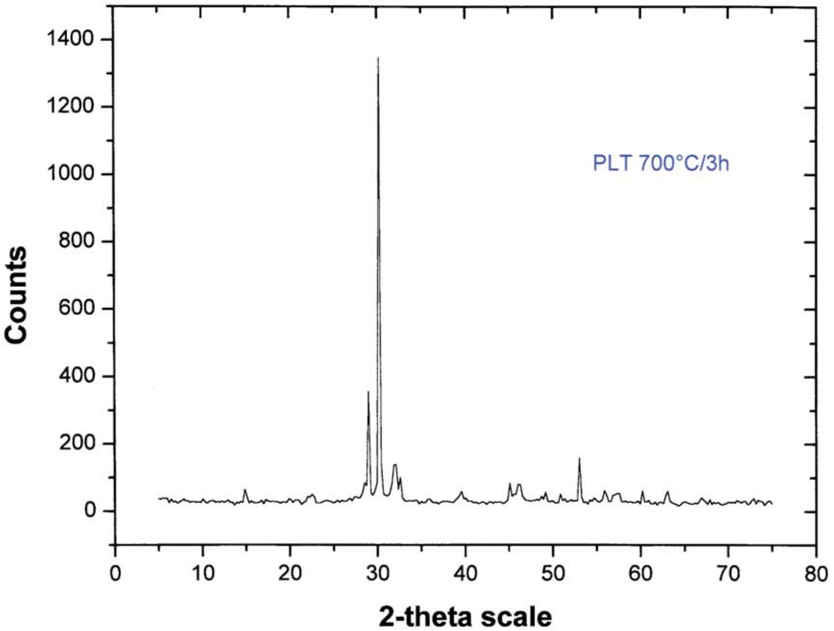

Fig. 3. X-ray diffraction pattern of powder calcined at 700 °C/3 h.

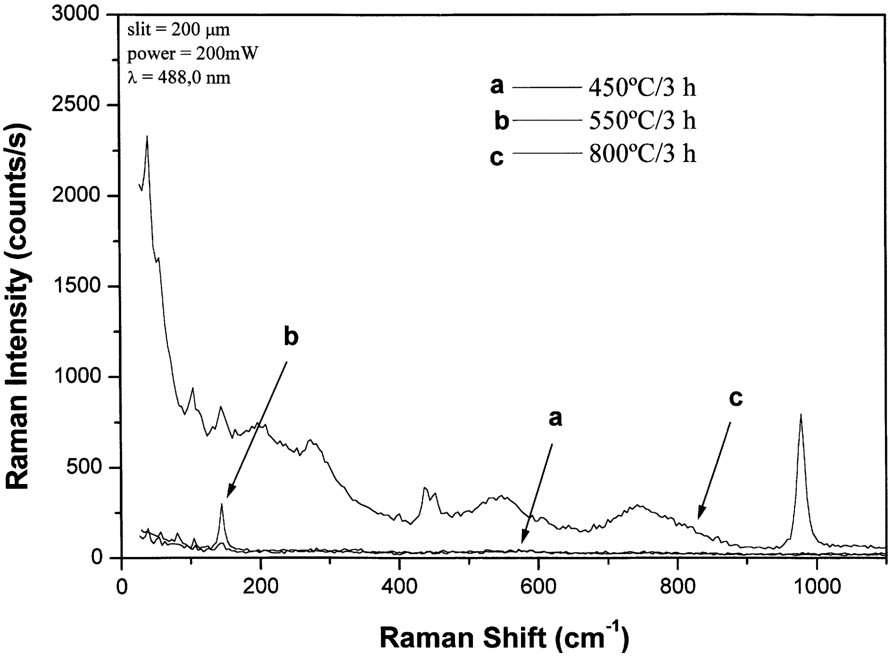

Fig. 4. Raman's observation of powder calcined at (a) 450, (b) 550, and (c) 800 °C/3 h.

450 °C (semi-crystalline powder). A broad absorption peak at 579 nm with an asymmetric curve was observed. The semi-crystalline powder does not show luminescence effect and small peaks of crystallinity were detected.

Crystalline PLT has a tetragonal ABO_3 perovskite structure with Ti ions in octahedral positions in the unit cell. The photoluminescence effect in amorphous powder could be attributed to emissions in the unit cell of Ti → O directly from the oxygen 2p orbital (valence bands) to the titanate 3d orbital (conduction bands). The presence of impurities caused a tail in the curve (asymmetric form). The electrons in the valence band of PLT, instead of getting excited to the conduction band directly, are first excited to some localized sensitizing centers which can be associated with some d-surface states in the forbidden gap. The electron polarons along with roles possibly trapped near the valence band then form an intermediate state, such as: self-trapped for a certain time.

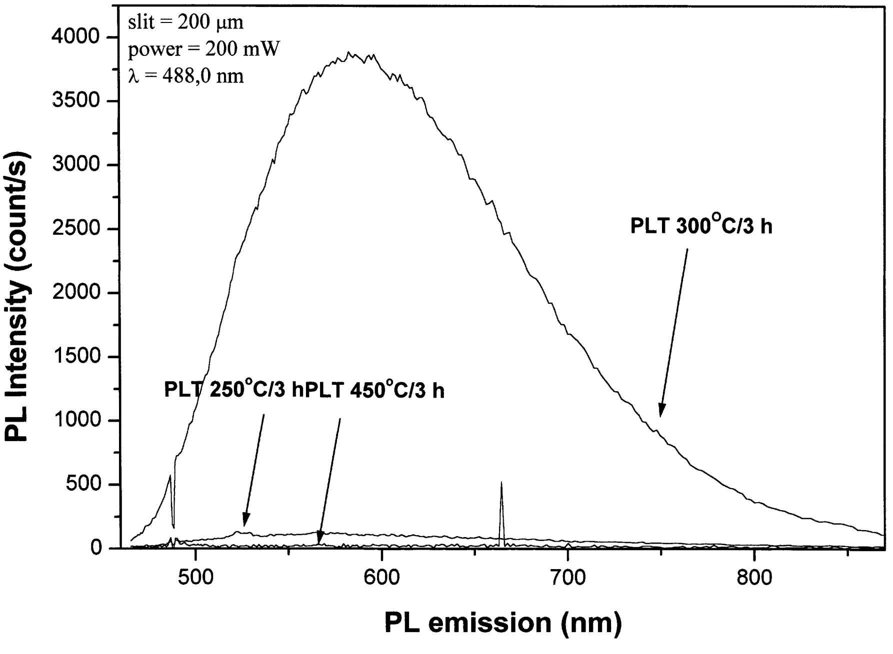

Fig. 5. PLT intensity vs. PL emission at 250, 300, and 450 °C/3 h.

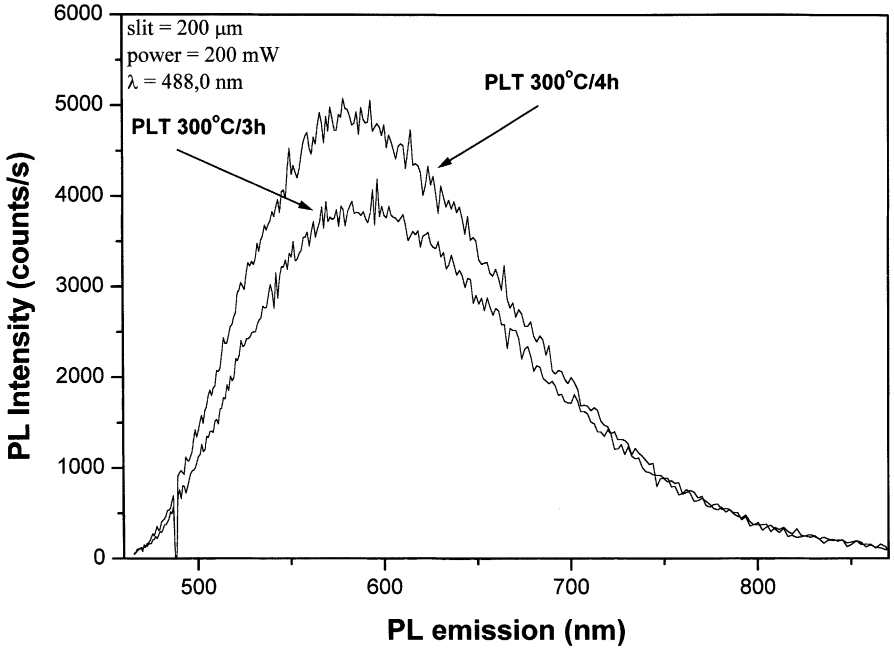

Fig. 6. PLT intensity vs. PL emission at 300 °C/3 h and 300 °C/4 h.

An optimization of processing of powder at 300 °C, Fig. 6 shows that an intense absorption peak of photoluminescence at 576 nm occurs after 4 h of calcination. This is attributed to an increase of defects formation such as vacancies and a disorder in the unit cell of the structure.

This non-defined structure with high concentration of defects caused a complex system of emission and depends only on the electronic structure of the surface states.

The increase of temperature from 300 to 350 °C, Fig. 7 shows an intense broad peak of photoluminescence at 350°/3 h. An increase of the time of calcination caused a strong decrease of photoluminescence effect. In this case the luminescence effect is caused by the amorphous state of structure. The increases of the time caused an organization of structure in the sense of crystallinity state of powder.

Comparisons by different calcining temperatures, Fig. 8 shows an evidence of photoluminescence effect caused by

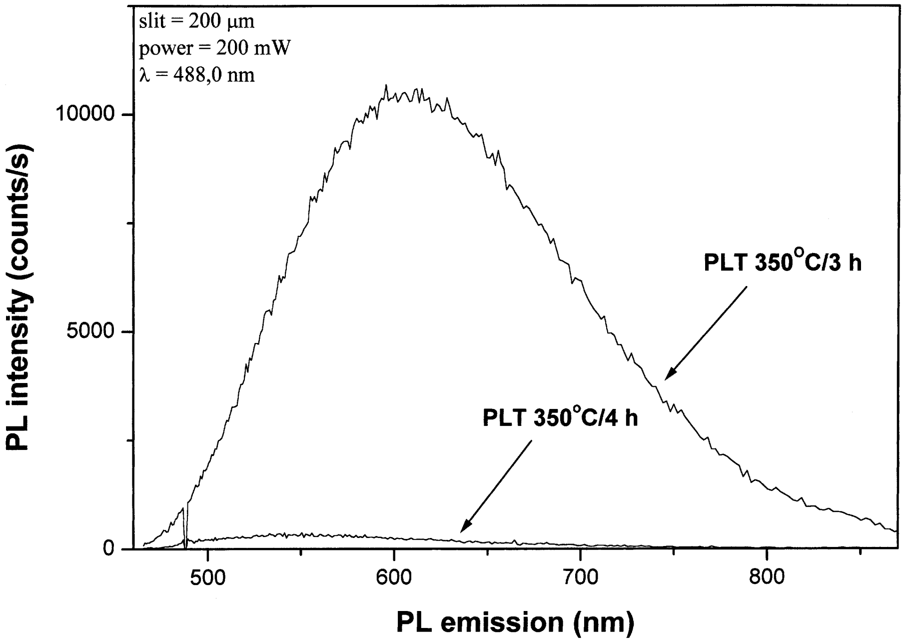

Fig. 7. PLT intensity vs. PL emission at 350 °C/3 h and 350 °C/4 h.

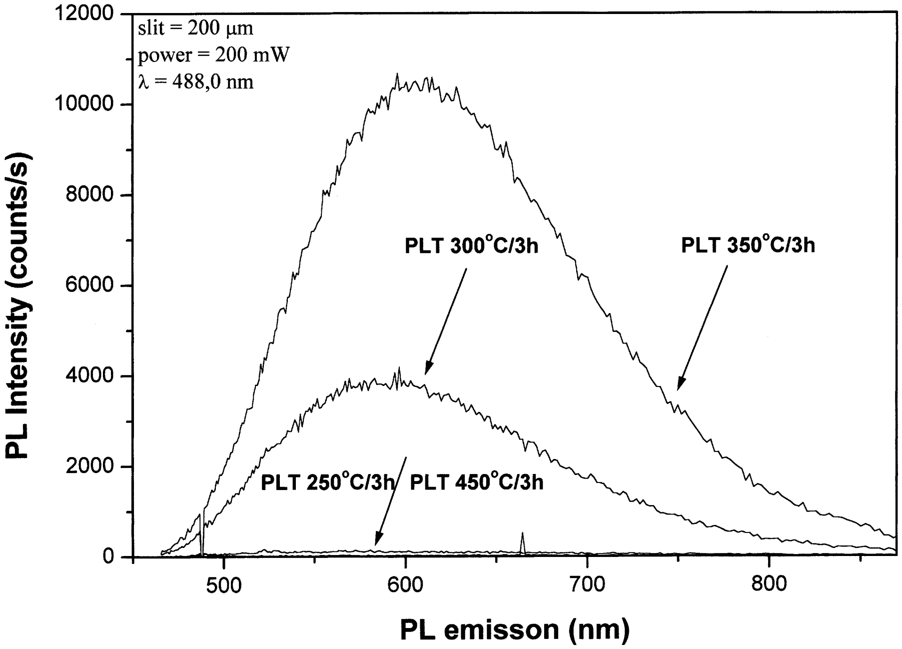

Fig. 8. PLT intensity vs. PL emission from 250 to 450 °C/3 h.

an amorphous state of powder. At 250°/3 h a high concentration of polymer, observed by IR shows that a luminescence effect does not occurs and is coincident with the analysis of semi-crystalline powder calcined at 450 °C/3 h. The photoluminescence effect is observed from 300 to 350 °C/3 h with a broad peak at 350 °C with 603 nm and at 300 °C with 584 nm. This could be explained by a definition of unit cell of structure.

According to Meng et al. the visible emission in nanocrystalline PT cannot be attributed to a Pb-transition or to a direct band-to-band transition. Thus a complex phenomenon of photoluminescence could be attributed to Ti → O emission. The results do not support further the visible emission model in nanocrystalline ABO_3 oxides: the electrons in the valence band of ABO_3 absorb photons and get excited to some localized sensitizing centers correlated with surface states in the forbidden gap, not directly to a conduction band.

The surface of the amorphous powder contains a noticeable quantity of Ti^{3+}–oxygen vacancies. The excitation of broadband emission is most effective in the high absorption coefficient region where practically all light is absorbed at the surface.

4. Conclusions

PLT phase calcined at different temperatures shows photoluminescence effect from 300 to 350 °C/3 h. The crystalline powder does not demonstrated same effect. Broad absorption peaks were observed at 584 nm (300 °C) and 603 nm (350 °C) in an asymmetric curve due to impurities presence. Emissions in the unit cell of Ti → O from oxygen 2p orbital (valence band) to the titanate 3d orbital (conduction bands) caused a luminescence effect in PLT.

Acknowledgements

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