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# Photoluminescence in amorphous PLZ

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## Abstract

Amorphous and crystalline powder of PLZ was prepared by using the polymeric precursor method. TGA-DSC (Thermal analysis and Differential Scanning Calorimetry) shows the decomposition of polymeric resin, an amorphous phase and the crystallization of powder. Raman scattering of powder shows an amorphous and semicrystalline phase at 450 and 550 °C, respectively. XRD (X-ray diffraction pattern) of powder shows high crystallinity at 700 °C/3 h. PL (Photoluminescence) analysis of powder at 300 °C/3 h shows a broad asymmetric peak at 585 nm and increases of calcining time led to intense peaks of PL at 300 °C/6 h. This emission could be attributed to Zr → O from the oxygen-2p orbitals to the zirconate-3d orbitals.

*Keywords:* Lead Zirconate; Photoluminescent materials; Amorphous materials

## 1. Introduction

Crystalline titanates and zirconates based materials are well-known compositions that presents photoluminescence effect. There has long been an interest in the perovskite type compounds because of their unusual dielectric, photoelectric, and optical properties. $ABO_3$ perovskite structure, such as PZT, PLZT, $Ba_{1-x}PbTiO_3$ (PBT), $BaTiO_3$ (BT), $SrTiO_3$ (ST) and others presents luminescence.

Recently, Pizani et al. [1] and others [2–4] reported the photoluminescence phenomena in amorphous material based on PT, PLT and ZT. The origin of the anomalous behavior has not been made clear yet.

The most plausible origin of visible luminescence in $ABO_3$ perovskite structure should be attributed to the $[BO_6]$ [4] center, because the s→p transition. The electronic configurations of $Zr^{4+}$ and $Ti^{4+}$ ions are 4 d° and 3 d°, respectively. Visible luminescence due to zirconium and titanium in this oxides is ascribed to LMCT (ligand-to-metal-charge-transfer) transitions in $[MO_6]^{n-}$.

Amorphous powder does not present long range order in the structure, however the unit cell is formed and charge transfer of Ti → O and Zr → O occurs. Amorphous titanate is formed by a Ti – O network and the charge of Pb cation must be compensated by the negatively charge non bridging oxygen (NBO) thus crystallization may eliminate defects, particularly the NBO which is probably the defect responsible for photoluminescence.

Crystalline zirconium titanate, PZ has an antiferroelectric $ABO_3$ structure. Optical studies in PZ material did not show an evidence of photoluminescence effect.

Recently, there has been a considerable interest in the fabrication of rare earth doped material for optically active waveguides and optoelectronic integrated circuits with silicon materials. Rare earth trivalent ions in some solid compounds emit light at characteristic wavelengths due to intra 4f or inter 4f–5d transitions [5].

The purpose of this work is a synthesis and optical characterization of amorphous Lead Lanthanium zirconium, PLZ obtained by using the Pechini method [6] of powder synthesis. Pechini was the first to demonstrate the use of polymeric precursor processing to form

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fine particles by fabricating a variety of complex oxides. This method has a distinct advantage over most other methods since very pure mixed oxides can be prepared.

## 2. Experimental procedure

Powder of $Pb_{1-x}La_xZrO_3$ (PLZ), where $x$ is the La molar fraction of 9 mol%, was prepared by using the polymeric precursor method, which is based on the chelation of cations (metals) by citric acid, in a water solution and ethylene glycol besides zirconium citrate in the present case. Lanthanium oxide and lead nitrate were added to the solution and lead oxalate was precipitated with an addition of oxalic acid until pH = 10. The raw materials used for the PLZ synthesis, as well as the origin are described in Table 1.

### 2.1. Characterization

The amorphous and crystalline character of the material was assessed by means of X-ray diffraction pattern (XRD) (Siemens, D5000) using a range of angles from $2\theta = 10°$ to 80°. The resin was analysed by infrared (IR) (Shimatzu model FT-IR 4200). Thermal analysis and differential scanning calorimetry (TGA-DSC) was carried out (Netszch, STA 409) in synthetic air up to 1200C and a heating rate of 5 °C/min.

Table 1
Raw materials used in the PLZ synthesis

| Material | Origin | % |
|---|---|---|
| Zirconium propoxide | Aldrich | 97.00 |
| Lead nitrate | Carlo Erba | 99.70 |
| Lanthanium oxide | Aldrich | 99.99 |
| Ethylene glycol | E. Merck | 99.50 |
| Citric acid | E. Merck | 99.50 |

#### 2.1.1. Photoluminescence effect

The photoluminescence spectra were performed by using a U 1000 Jobin-Yvon double monochromator coupled to a cooled GaAs photomultiplier and conventional photon counting system. 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.

## 3. Results and discussion

### 3.1. Phase formation

Figs. 1. and 2 show a TGA-DSC of polymeric resin with high weight loss from 100 to 580 °C. A differential of DSC curve shows different events. A negative peak close to 400 °C is related to a decomposition of C=O stretching for the ester groups (R – COO - R). These groups are formed during the polyesterification reaction between ethylene glycol and citrates. A positive peak at 520 and 550 °C is related to long range order (crystallization) of powder. The X-ray diffraction pattern

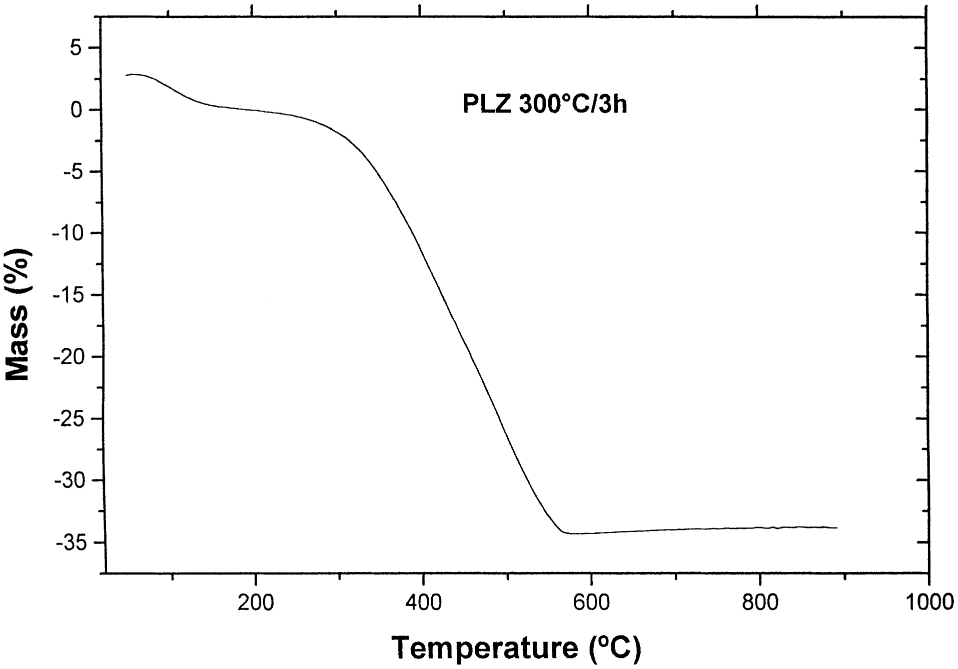

Fig. 1. TGA analysis of polymeric resin.

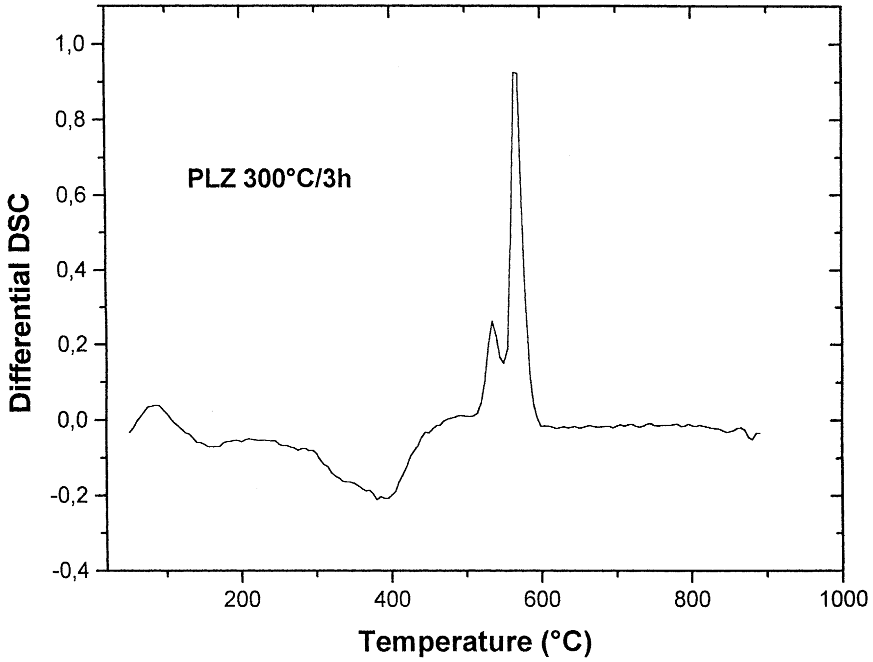

Fig. 2. DSC analysis of polymeric resin.

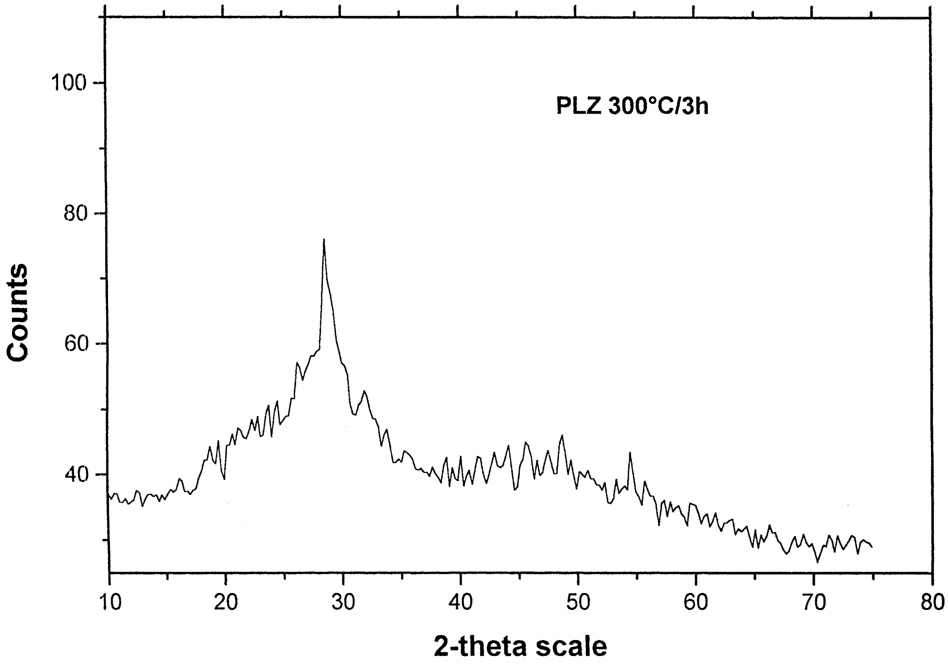

Fig. 3. X-ray diffraction pattern of powder calcined at 300C/3 h.

(XRD), Fig. 3 of powder calcined at 300 °C/3 h shows an amorphous phase. XRD analysis, Fig. 4 at 550 °C/3 h shows a crystalline phase presence with broad peaks indicating a PLZ phase formation.

Fig. 5 shows a XRD of powder calcined at 700 °C/3 h of PLZ phase with high crystallinity grade. Small peaks of PbO phase are caused by an excess of PbO during calcination. Raman scattering of powder, Fig. 6 calcined from 450 to 800 °C/3 h shows a formation of amorphous phase at 450 °C/3 h and a semicrystalline phase at 550 °C/3 h demonstrating the same results relative to XRD data. Intense peaks of Raman were observed at the powder calcined at 800 °C/3 h indicating that a crystalline phase was formed.

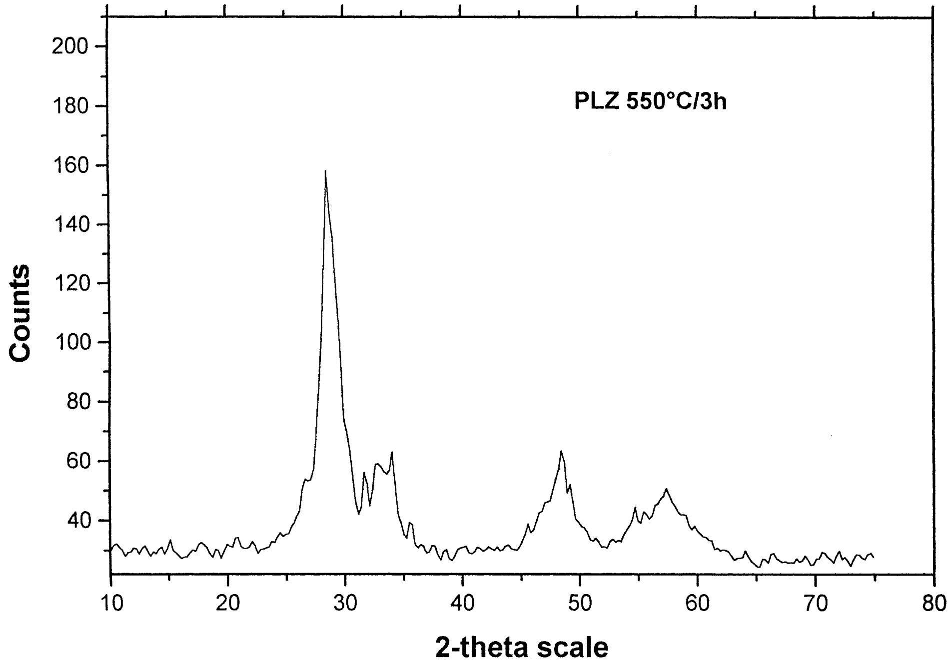

Fig. 4. X-ray diffraction pattern of powder calcined at 550 °C/3h.

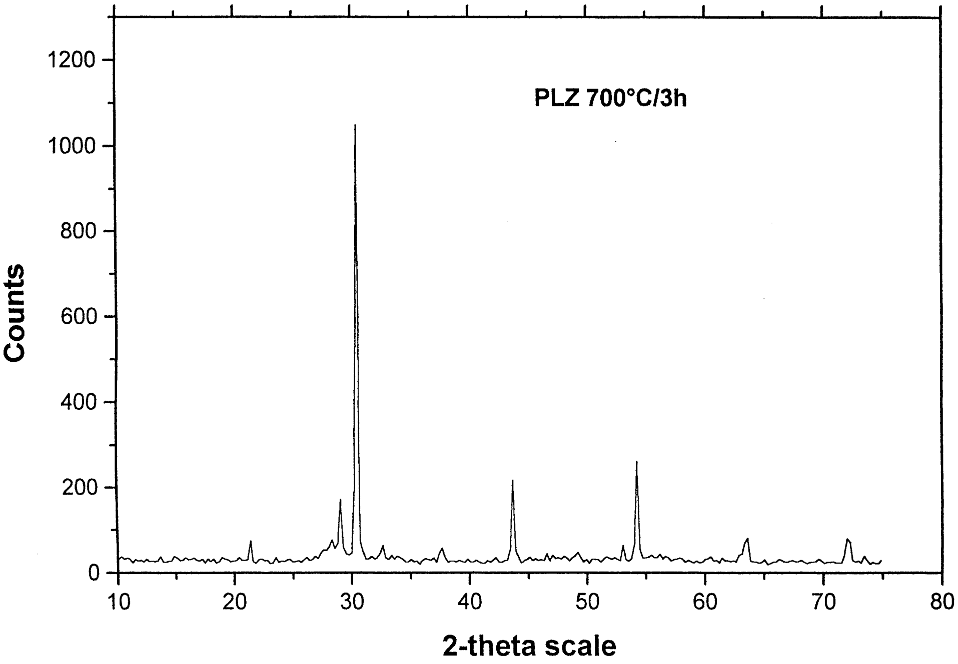

Fig. 5. X- ray diffraction pattern of power calcined at 700 °C/3 h.

### *3.2. Photoluminescence measurements*

Analysis of powder calcined from 250°to 450 °C/3 h, Fig. 7 shows photoluminescence (PL) effect at 300 °C/3 h. A broad asymmetric peak of PL at 585 nm was observed. Measurements of luminescence spectra of $ZrO_2$ at 10 K as a reference show a peak at 540 nm. At 250 °C during 3 h a high concentration of polymer and products of decomposition does not promote luminescence effect. The same results were observed at 450 °C/3 h coincident with a formation of small quantities of crystalline phase observed by Raman.

Recent investigations by Pizani et al. [1] show PL in amorphous powder and crystalline thin film based on

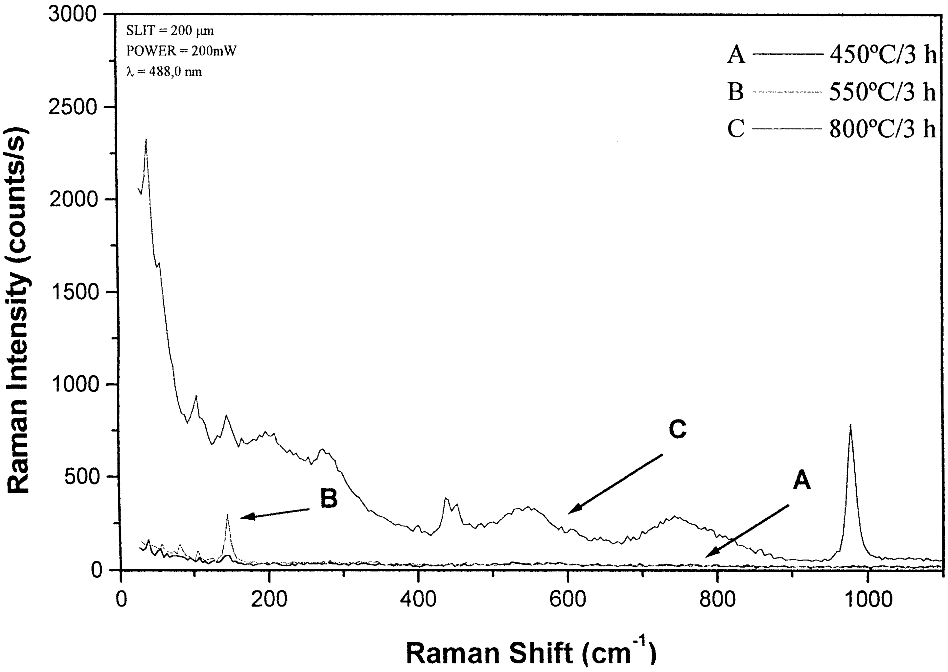

Fig. 6. Raman scattering of powder calcined from 450° to 800 °C/3 h.

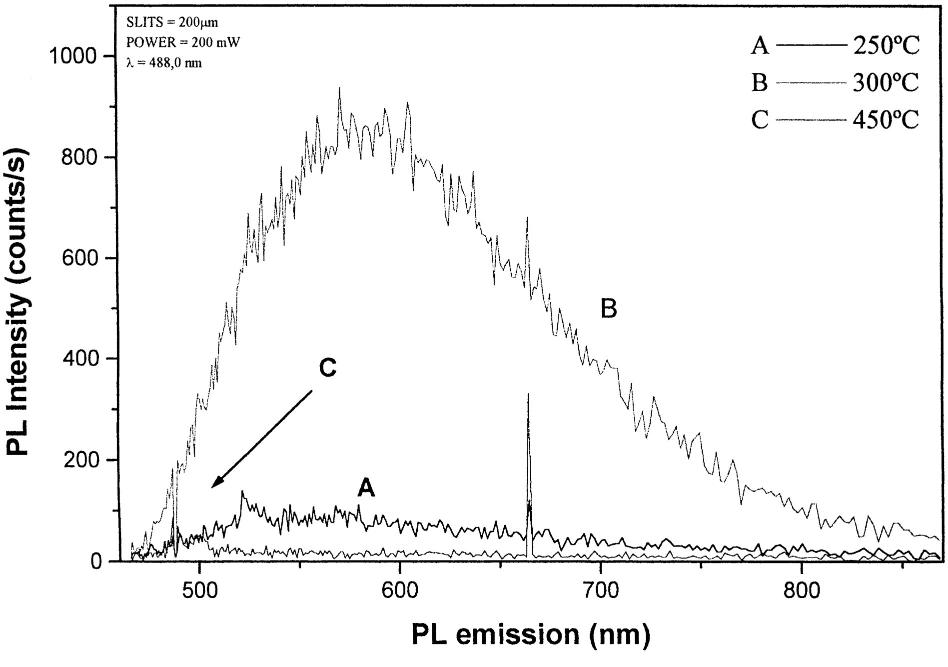

Fig. 7. Photoluminescence of powder calcined from 250° to 450 °C/3 h.

lead titanium (PT). Freitas et al. [7] studied amorphous lead lanthanium titanium (PLT) obtaining broad peaks of photoluminescence calcining powder at 300 °C/3 h.

PZ has an antiferroelectric, $ABO_3$ structure and the PL effect could be attributed to emissions of Zr → O directly from the oxygen-2p orbitals (valence band) to the zirconate-3d orbitals (conduction bands). This phenomena are similar to those ascribed by Freitas et al that consider the electrons in the valence band of PLT instead of getting excited to some localized sensitizing centers which can be associated with some d-surface states in the forbidden gap.

As in the case of emission in PLZT the PLT with $ABO_3$ structure generally could give photoluminescence

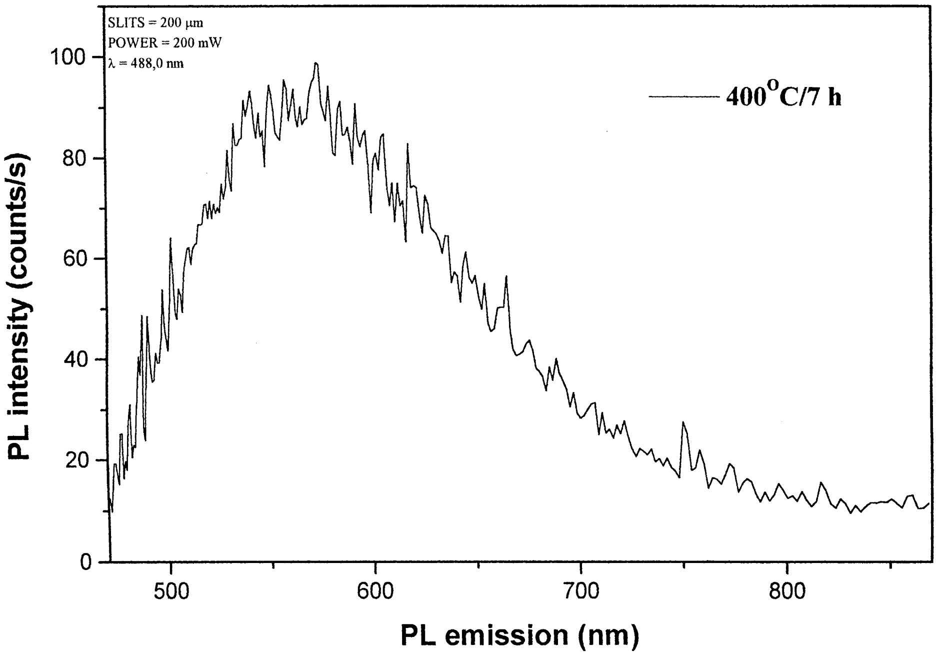

Fig. 8. Photoluminescence of powder calcined at 400 °C/7 h.

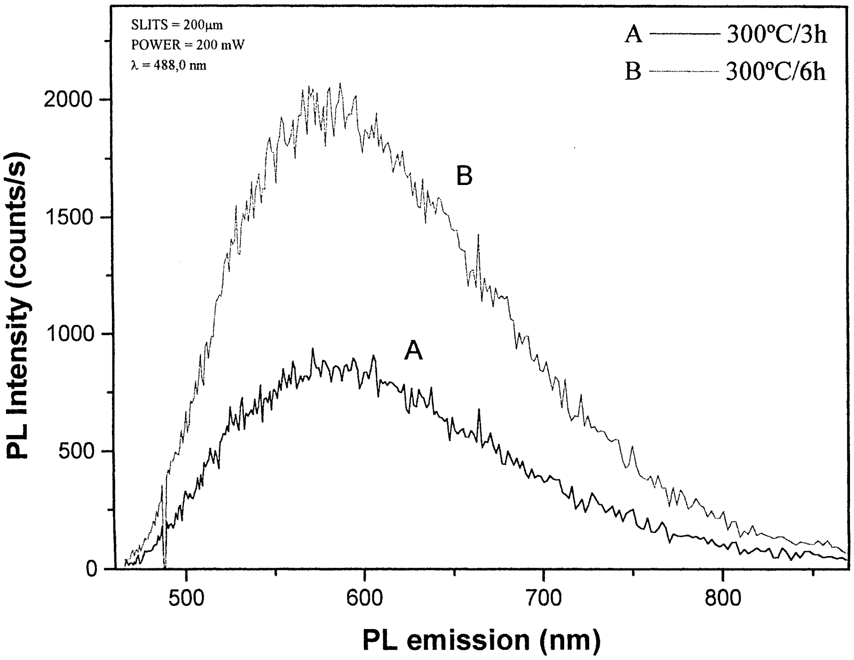

Fig. 9. Photoluminescence of powder calcined at 300 °C/3 h and 300 °C/6 h.

due to ions at A- and B-sites in addition, we have to consider the presence of color centers (including vacancies of $V_O$, $V_{pb}$ etc), donor-acceptor pairs and imputities (Fe, Mn, Co, Ni etc) centers. They occupy either the substitutional site ([$AO_{12}$] or [$BO_6$] complex) and/or the interstitial site. As a acceptor state formation substitutions of $La^{3+}$ in $Pb^{2+}$ positions caused Pb vacancies in [$AO_{12}$] complex. The presence of trivalent $La^{3+}$ and others impurities causes a number of oxygen vacancies, forming [$ZrO_2$] type defects in the unit cell.

The most plausible origin of visible luminescence in the unit cell should be attributed to the [$BO_6$] center, because of the s → p transition due to the $PbO_{12}$ center observed usually in the ultraviolet to blue spectral region. Visible luminescence due to $Zr^{4+}$ in these oxides is ascribed to LMCT (ligand-to-metal-charge-transfer) transitions in $[MO_6]^{n-}$, as in the case of emission in $Bi_2WO_6$ [8,9]. The same type of LMCT transitions in luminescence of $[MO_4]^{n-}$ type are well known as scheelite-type compounds (e.g. $YVO_4$) and also in transition metal ions-doped sol–gel silica glasses (e.g. $SiO_2$:$Ti^{4+}$).

Fig. 8 shows the PL effect of powder calcined at 400 °C/7 h with a broad peak at 576 nm. The decreases of PL could be attributed to increases of long-range-order of structure. An organization of structure caused decreases of defects concentration, such as vacancies and decreases the visible emission.

Increases of calcining time of powder, Fig. 9 from 300 °C/3 h to 300 °C/6 h increase the peak of PL with emission at 575 nm. Thermal treatment by a long time caused defects formation due to charge motion into the structure.

In PLZ the pseudocubic perovskite unit cell consists of a small body-centered metal ion (zirconium), large metal ions (lead) on the corners of the cubic lattice, and face-centered oxygen ions. The oxygens have octahedralsymmetry about the central atom. The valence and conduction bands have been calculated for similar ferroelectric crystals (i.e barium titanate and strontium titanate [10,11]. The conduction band consists of primarily of empty $t_{2g}$ titanium bands while the valence band consists of filled oxygen 2p states.

The luminescence effect is independent of ferroelectricity state. Different materials with ferroelectric – $ABO_3$ structure showed PL effect at room temperature. For crystalline $PbTiO_3$ is found to be similar to that of $BaTiO_3$ or $SrTiO_3$ with all of them showing a wide structureless band although they belong to different structures, that is for $PbTiO_3$ exhibits a tetragonal ferroelectric phase while for both $BaTiO_3$ and $SrTiO_3$ show a cubic paraelectric phase. This implies that the visible emission bands of $BaTiO_3$, $SrTiO_3$ and $PbTiO_3$ are ferroelectricity independent. Thus, experimental evidence shows that the observed effect could be attributed principally to amorphous state of powder.

## 4. Conclusions

Amorphous and crystalline powder was synthesized by using the Pechini method. Intense peaks of photoluminescence were observed at 585 nm at 300 °C/3 h and 575 nm at 300 °C/6 h. This phenomena could be attributed to emissions of Zr → O from the oxygen-2p orbitals (valence band) to the zirconate-3d orbitals (conduction bands). The asymmetry of curve is due to presence of defects and impurities. Visible luminescence due to $Zr^{4+}$ is ascribed to LMCT transitions in $[MO_6]^{n-}$.

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