Research & Reviews: Journal of Chemistry

e-ISSN: 2319-9849
p-ISSN: 2322-00

# Preparation of Zinc Oxide Nanomaterial using Unsymmetrical Schiff Base Complexes

**Maldhure AK[1*] and Aswar AS[2]**

[1]Department of Chemistry, Arts, Commerce and Science College, Kiran Nagar, Amravati, India

[2]Department of Chemistry, Sant Gadge Baba Amravati University, Amravati, India

**Research Article**

Received date: 26/05/2018;

Accepted date: 20/06/2018;

Published date: 25/06/2018

*For Correspondence:

Maldhure AK, Department of Chemistry, Arts, Commerce and Science College, Kiran Nagar, Amravati, India, Tel: 09822939260

E-mail: atishkmaldhure@yahoo.co.in

Keywords: Unsymmetrical schiff base complexes, Nanomaterial, Zinc oxide, Powder X-ray diffraction.

## ABSTRACT

The unsymmetrical Schiff base Zn(II) complexes $Zn(L)(H_2O)_2$, where L is the unsymmetrical tetra-dentate Schiff base ligands of N-(5-bromo-2-hydroxy acetophenone)-N'-(2-hydroxy acetophenone) ethylenediamine ($L_1$) and N-(3,5-dibromo-2-hydroxy acetophenone)-N'-(2-hydroxy acetophenone) ethylenediamine ($L_2$) were synthesized and characterized by physico-chemical and spectroscopic methods. Zinc oxide nanomaterial was obtained followed by calcination at 260°C. The structures of the nano-sized compounds were characterized by X-ray powder diffraction and scanning electron microscopy. The thermal stabilities of the complex and nano-sized ZnO particles were studied by thermogravimetric analysis.

## INTRODUCTION

Schiff bases are the most important and widely studied class of chelating ligand due to the wide possibility of synthesizing a large number of Schiff bases from a single aldehyde or an amine by a mere alteration of the substituent's in them. Schiff base ligands are considered "privileged ligands" because they are easily prepared by the direct condensation of primary amines with aldehydes or ketones under specific conditions and thus they contain an azomethine group (>C=N-). Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most transition metals. Several transition metal Schiff base complexes have been found to possess interesting biological properties and they have been used in the preparation of many potential drugs and are known to possess a broad spectrum of biological and catalytic activities [1-8]. Recently, several groups used metal complexes as a precursor for preparation of metal oxide nanoparticles by various methods. Among various techniques, preparation of metal oxide nanoparticles solid-state thermal decomposition of transition metal complexes is one of the best method, because it is inexpensive (economical) and does not use toxic solvent (pollution free) and surfactant route and is much faster, whereas process conditions, particle size and purity can be easily controlled [9,10]. In the present paper, we report the synthesis of ZnO nanomaterial from Zn(II) Schiff base complexes by solid-state thermal decomposition method.

## EXPERIMENTAL

The unsymmetrical Schiff base Zn(II) complexes of the unsymmetrical tetra-dentate Schiff base ligands of N-(5-bromo-2-hydroxy acetophenone)-N'-(2-hydroxy acetophenone) ethylenediamine (L1) and N-(3,5-dibromo-2-hydroxy acetophenone)-N'-(2-hydroxy acetophenone) ethylenediamine (L2) **(Figure 1)** were synthesized according to reported method and characterized by physico-chemical and spectroscopic methods [11,12].

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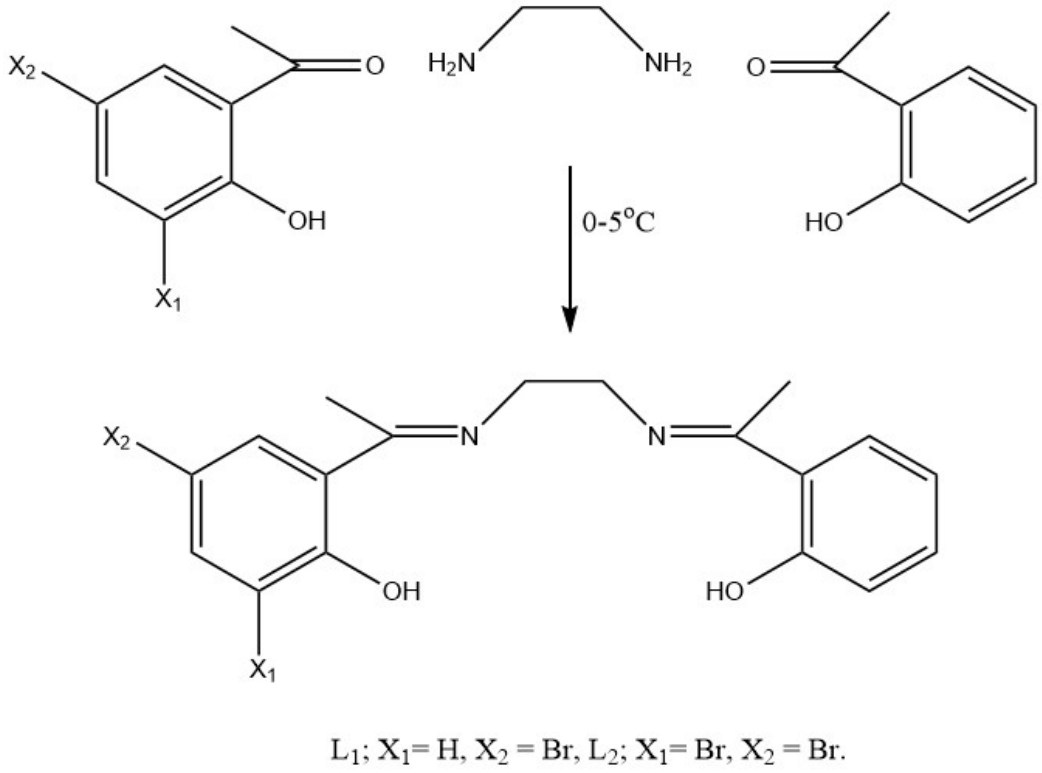
All reagents and solvents for synthesis were commercially available and used as received. The metal content in the complexes was analyzed by standard method. The analysis of carbon, hydrogen and nitrogen were performed on Carlo Erba 1108 elemental analyzer at Central Drug Research Institute (CDRI), Lucknow, India. The infrared spectra were obtained in KBr pellets on Shimadzu IRAFFINITY-1 at Government College of Pharmacy, Amravati, India. $^1$H NMR spectrum of ligand was obtained using a Bruker Auance-II 400 NMR spectrophotometer in a mixed solvent (DMSO +$CdCl_3$) at SAIF Punjab University, Chandigarh. The Electronic spectra of the complexes were recorded on Cary-60 UV spectrophotometer. Magnetic susceptibilities were determined on a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were calculated from Pascal's constants. The solid state D.C. electrical conductivity of compounds was measured by Zentech Electrometer in their compressed pellet form over 313-403 K temperature range. TG analysis of the complexes was carried out on Perkin Elmer TG-2 thermo-balance in ambient air with a heating rate of 10°C per minute. Metal contents of the complexes were analyses gravimetrically after decomposing the complexes with a mixture of $HClO_4$, $H_2SO_4$ and $HNO_3$ and then igniting to metal oxide. The powder XRD was recorded at VNIT, Nagpur, India.




$L_1$; $X_1$= H, $X_2$ = Br, $L_2$; $X_1$= Br, $X_2$ = Br.

**Figure 1.** Synthesis of Unsymmetrical Schiff Base ligand.

### Synthesis of Manganese (II), Nickel (II) and Zinc (II) Complexes

To a hot DMF-EtOH solution (50:50) (25 ml) of ligand (2 mmol), a hot ethanolic mixture of the appropriate metal salt (2 mmol) was added with continuous stirring. The resulting reaction mixture was heated/reflux for 4-5 h. On cooling to room temperature, the solid complexes were filtered, washed thoroughly with ethanol, DMF and Petroleum ether to remove unreacted ligand and metal salts and dried (Yield: 60-65%).

### Synthesis of ZnO Nanomaterial

The precursor of Zn(II) complex (76.2 mg, 0.2 mmol) was dissolved in 1.4 mL of Oleic acid and formed a greenish black solution. This clear solution was heated to 260°C for 2 hours under air atmosphere. At the end of the reaction, a black precipitate was formed. A small amount of toluene and a methyl alcohol (1: 2) were added to the reaction solution and ZnO nanoparticles were separated by centrifugation. The dark solid obtained was washed with EtOH and dried in vacuum as in Scheme 1.

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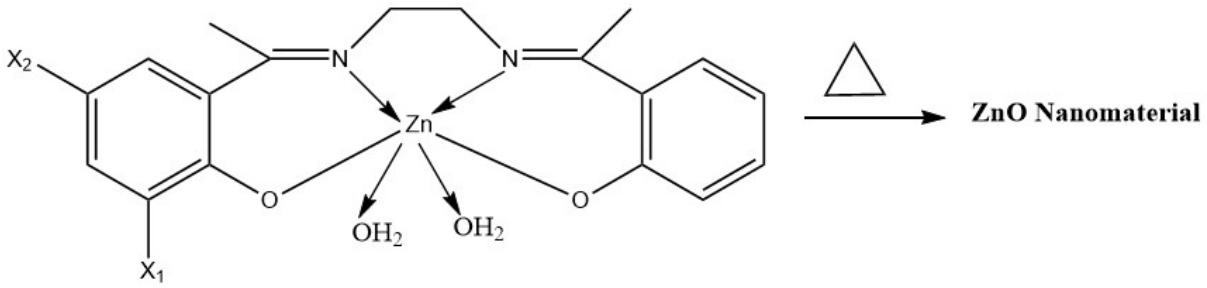


$L_1$; $X_1$= H, $X_2$ = Br, $L_2$; $X_1$= Br, $X_2$ = Br.

**Scheme 1.** EtOH in vacuum.

## RESULTS AND DISCUSSION

All the metal complexes are colored solids, non-hygroscopic, air stable and insoluble in common organic solvents but sparingly soluble in DMF and DMSO respectively. The elemental analysis shows 1:1 metal to ligand stoichiometry for all the complexes.

### IR Spectra

The IR spectra of the complexes have been compared with ligand in order to determine the coordination sites. Reaction between $N_2O_2$ donor Schiff base ligands and zinc(II)chloride yielded Zn(II) unsymmetrical Schiff base complex formulated as $[ZnL(H_2O)_2]$. The characteristic vibrational frequencies have been identified by comparing the spectra of complex with that of parent ligands and literature value of absorption of simple type of compound. The shift of ν(C-O) (phenolic) band to 1305- 1338 cm-1 in the spectra of complexes **(Figure 3)** indicating the co-ordination of phenolic oxygen atom to the metal ion [13,14]. The strong band observed due to ν(C=N) stretch in ligand spectrum has been shifted to lower frequency 1535- 1541 cm-1 upon co-ordination [15]. The Zn (II) complexes were found to diamagnetic and do not show any d- d transition as expected for d10 system. The powder X-ray diffraction indicates crystalline nature of Zn (II) complex (Figure 2). The Zn(II) ion in octahedral environment with the ligand and two neutral water ligand also confirmed by TG analysis.

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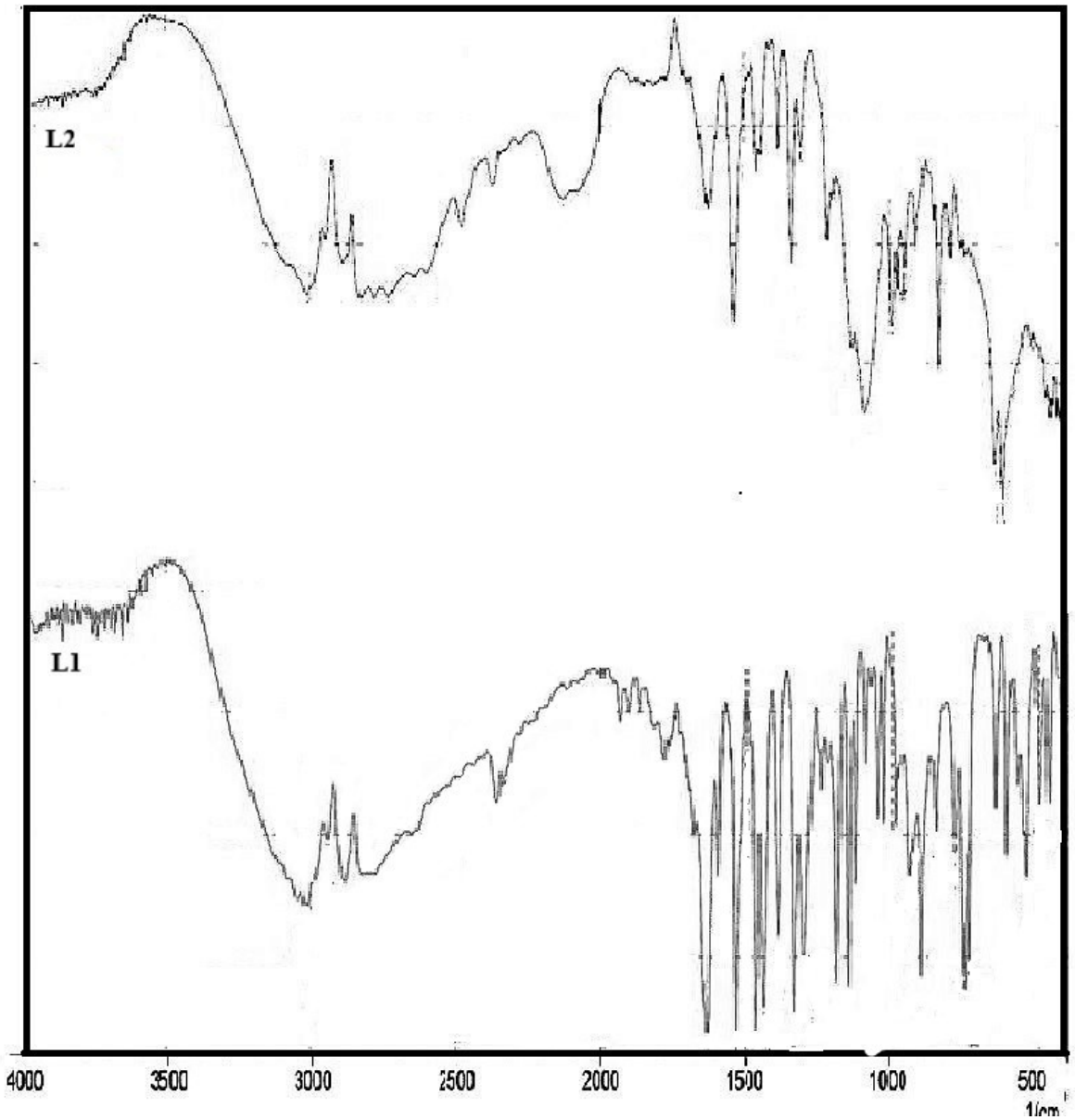


**Figure 3.** IR Spectra of Zn(II) Complexes.

ZnO nanoparticles can be synthesized from the decomposition of the Zn(II) complex precursor in oleic acid under air atmosphere. The IR spectrum of ZnO nanoparticle **(Figure 4)** exhibits band at about 617 $cm^{-1}$ that can be assigned to the stretching mode of ZnO. The nanoparticle size of metal oxides measured by XRD and SEM indicate that the size of Metal oxide nanoparticles was about 300-500 nm.

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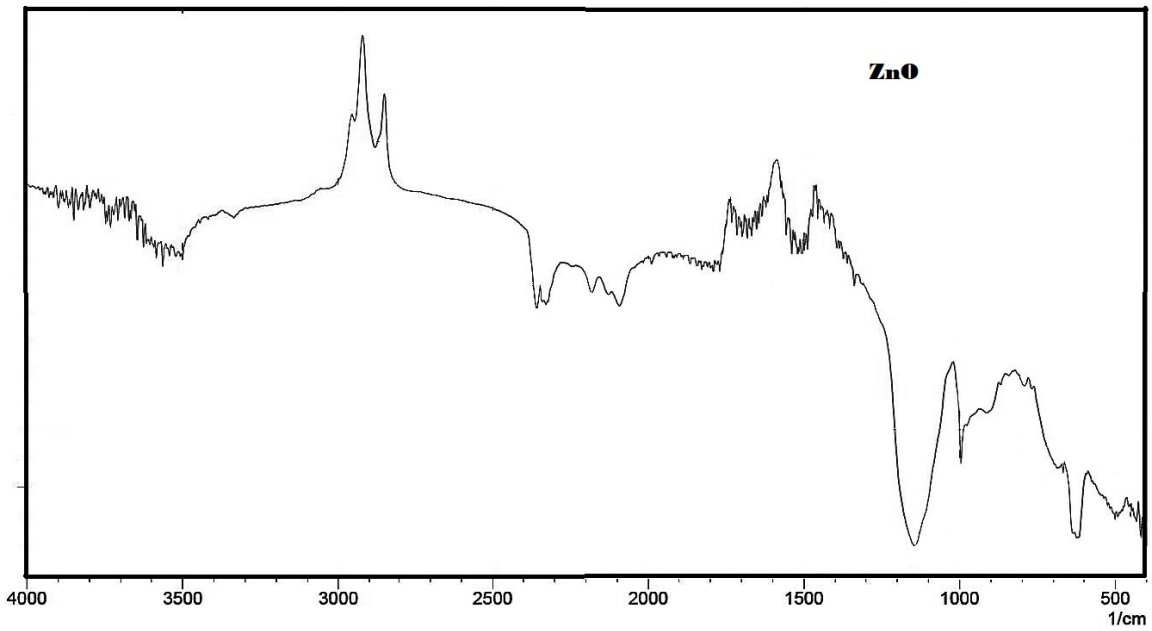


**Figure 4.** IR Spectra of ZnO.

The TG curve of Zn(II) Complexes **(Figure 5)** indicates that the compound is stable up to 140°C. Removal of two coordinated water takes place in the range 140-280°C. (The weight loss observed 9.46 Calculated 9.44%). Rapid weight loss has been observed around 300°C presumably due to decomposition of organic constituent of the complex molecule. The decomposition continues up to 650°C as indicated by the consistency in weight in the plateau of thermogram.

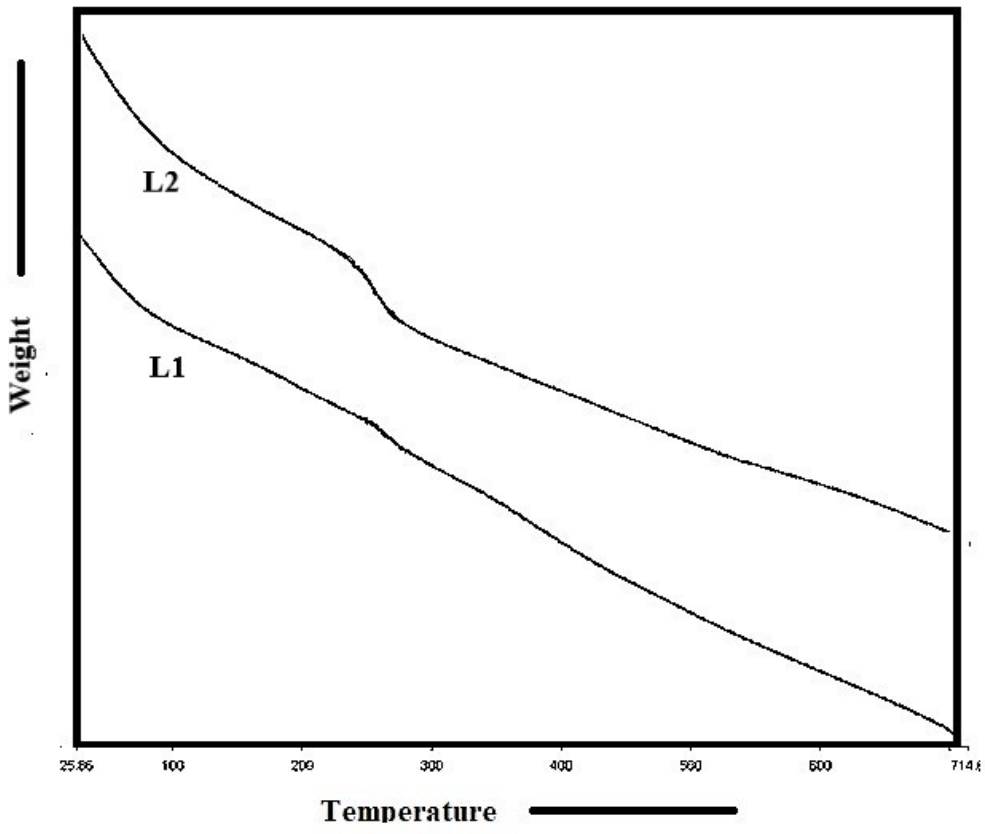


**Figure 5.** TGA graph of Zn(II) complex.

e-ISSN: 2319-9849
p-ISSN: 2322-00

ZnO nanoparticles can be synthesized from the decomposition of the Zn(II) complex precursor in oleic acid under air atmosphere. The IR spectrum of ZnO nanoparticle exhibits band at about 557 $cm^{-1}$ that can be assigned to the stretching mode of ZnO. The nanoparticle size of metal oxides measured by XRD and SEM indicate that the size of Metal oxide nanoparticles was about 300-500 nm (Figure 6 and 7).

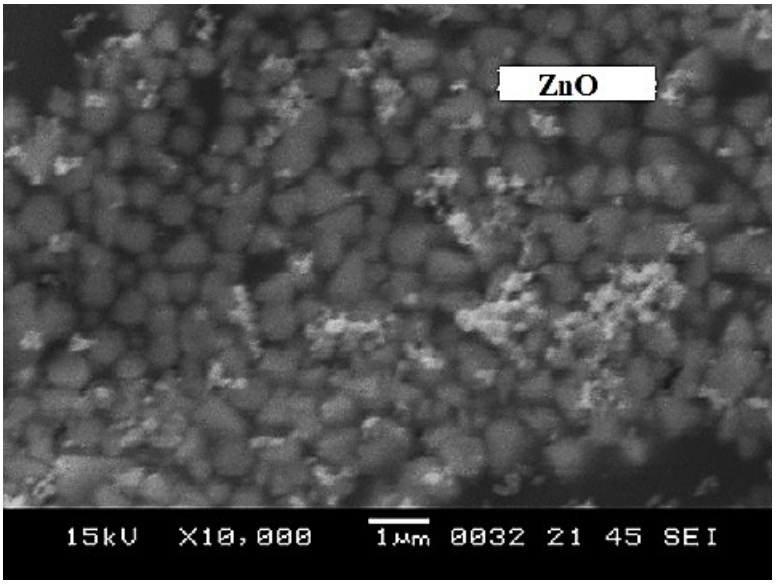


**Figure 6.** SEM of ZnO nanomaterial.

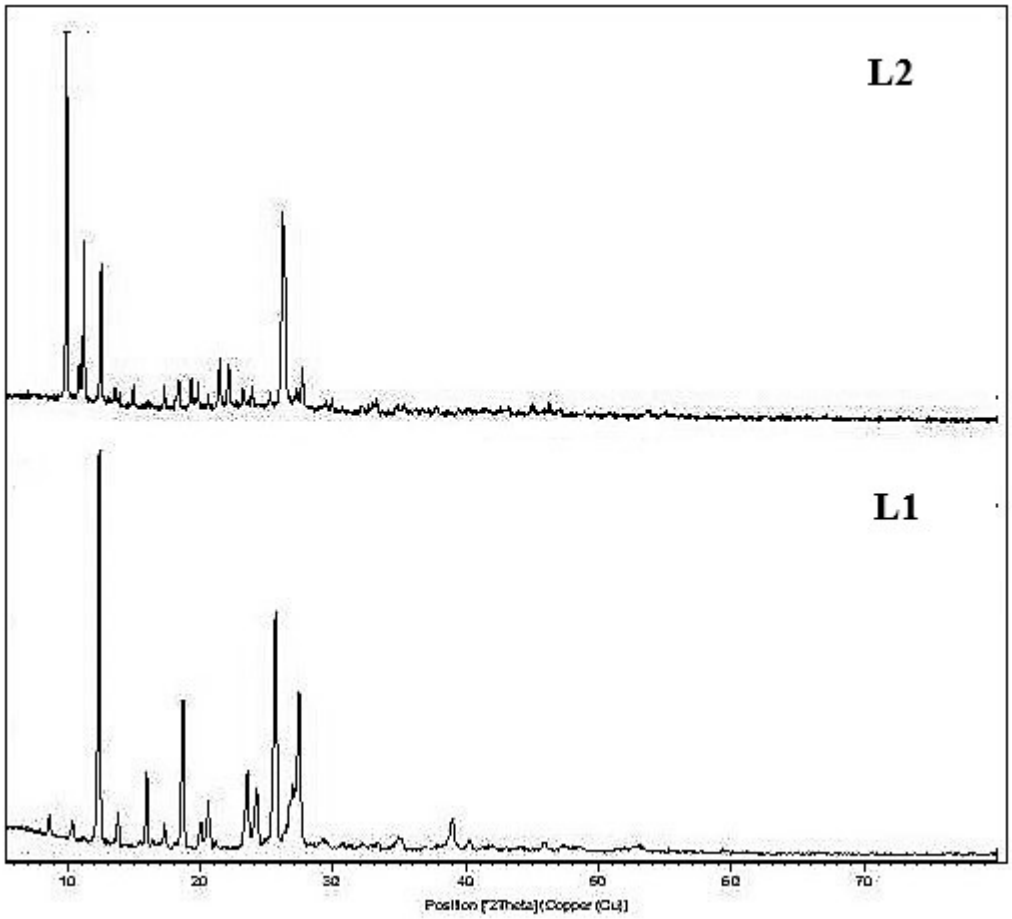


**Figure 7.** XRD of ZnO nanomaterial.

e-ISSN: 2319-9849
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## CONCLUSION

In the present paper, Schiff base Zn(II) complexes of the unsymmetrical tetra-dentate Schiff base ligands N-(5-bromo-2-hydroxy acetophenone)-N'-(2-hydroxy acetophenone) ethylenediamine ($L_1$) and N-(3,5-dibromo-2-hydroxy acetophenone)-N'-(2-hydroxy acetophenone) ethylenediamine ($L_2$) were synthesized and characterized. The solid-state thermal decomposition method is an easy, safe and suitable for high purity production for the preparation of nanoparticles. This method also has potential advantages, including operational simplicity, no need for solvent, low energy consumption.

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