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Spectral, morphological, linear and nonlinear optical properties of nanostructured benzimidazole metal complex thin films

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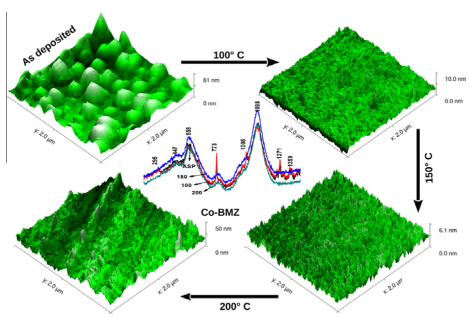
HIGHLIGHTS

- Computational studies ensure the potentiality of Benzimidazole metal complexes towards third order NLO applications.
- Annealing improves the surface uniformity and reduces the optical scattering losses.
- Thermal induced degradation of both the metal complex thin films have been observed by Raman spectroscopy.

GRAPHICAL ABSTRACT



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ABSTRACT

Metal organic materials are widely investigated to find their suitability for nonlinear optical applications due to the advantage of combined organic and inorganic properties. In this work benzimidazole based metal organic thin films of dichlorobis (1H-Benzimidazole) Co(II) and dichlorobis (1H-Benzimidazole) Cu(II) were deposited by chemical bath deposition method. The deposited films were annealed at 100, 150 and 200 °C to investigate the effect of annealing on the properties of thin films. Surface homogeneity of the films was increased with the annealing temperature due to the surface diffusion of the films and the same was evidently shown by Raman spectroscopy and Atomic Force Microscopy studies. But annealing the films at 200 °C yielded bulk patches on the surface due to the distortion of molecules. Linear and nonlinear optical properties of the films annealed at 150 °C showed relatively higher transmittance and improved nonlinear optical properties than the other as prepared and annealed samples.

Introduction

Nonlinear optical (NLO) materials with larger hyperpolarizabilities have been investigated for applications in optical switching, signal processing and optical limiting [1,2]. Organic π conjugated materials have been widely investigated due to their better nonlinear optical susceptibilities than the inorganic NLO materials. Organic materials offer low cost fabrication and flexible design possibilities [3,4]. But, the main disadvantages of organic materials are lack of good thermal and mechanical durabilities, and exhibit more optical scattering losses. To overcome these difficulties metal organic materials are considered as the better alternatives due to their versatile molecular configuration, which often enhances the physical properties and provides high laser damage threshold than their organic counterparts [3]. The NLO properties of these materials can be tuned by altering the metal-ligand combinations [5,6]. Depending on the electronegativity, metal centers in the

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metal-organic systems can create additional energy levels and electronic transitions other than the $\pi-\pi$ transitions [7]. Especially, the metal ions introduced in a π-conjugated system largely contribute to the charge transfer mechanism between metal and ligand, which can enhance the third order nonlinear optical susceptibility of the materials [8]. NLO materials can be prepared in various forms such as crystals, nanoparticles, polymer composites, thin films, etc. Most often, thin films are considered as suitable candidates for device applications due to their portability, compatibility with silicon photonics and planar waveguides, and their low optical path lengths, which considerably reduces the scattering losses. [9]

Benzimidazole (BMZ), an organic small molecular compound falls under the heterocyclic aromatic category, is well known for its anti-microbial activities [10]. In the recent past, BMZ and its derivatives gain much interest in materials science regime and investigated for the optical, gas, dye sensing and cancer treatment related applications [11–13]. Especially, it is identified as one of the potential second harmonic generation (SHG) materials since it possesses 4 times the SHG efficiency of the standard potassium dihydrogen phosphate (KDP) crystal [14]. Several reports on the coordination behaviour of BMZ with transition metal ions evidently show the ability to tune its properties. Previous works report that incorporation of metal ions in BMZ medium enhances its optical, magnetic and antimicrobial properties [15,10,16]. Further it was reported that the enhancement in the third order nonlinearity can be achieved by the incorporation of Cu or Co metal ions in an organic medium [17]. In this context, we report on the deposition of thin films of dichlorobis (1H-Benzimidazole) cobalt(II) (Co-BMZ) and dichlorobis (1H-Benzimidazole) copper(II) (Cu-BMZ) complexes and characterized them to explore their linear and nonlinear optical properties as a function of annealing temperature.

Materials and methods

All the reagents used in the deposition of Co-BMZ and Cu-BMZ films were purchased from Merck Chemicals. Microscopic glass slides (Labtech) were used as the substrates for film deposition. In the preparation of both the metal complex films, respective metal chlorides ($CoCl_2.6H_2O$ and $CuCl_2.2H_2O$) and ligand (BMZ) were taken in 1:2 ratio. Mixture of methanol and dimethylformamide taken in 3:1 ratio was employed to deposit Cu-BMZ films whereas Co-BMZ films was deposited from ethanol. For depositing films, two glass substrates were fused together by using a sellotape and dipped into the precursor solution, refluxed for 7 h at 70 °C. During the deposition process, the Cu-BMZ solution turns from pale green to dark green and Co-BMZ solution turns to dark blue from pale whitish blue. Then, the deposited films were removed from the solution and dried in a hot air oven at 50 °C for 2 min. The as deposited samples (ASP) were annealed at 100°, 150° and 200 °C (hereafter the samples are termed as 100, 150 and 200) in the open air atmosphere for 2 h, to study the effect of annealing temperature on the surface morphology of the films.

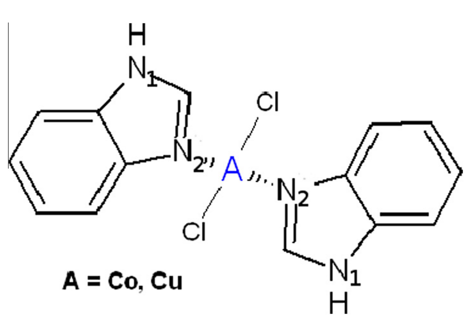

Fig. 1. Chemical Structure of Co-BMZ and Cu-BMZ complexes.

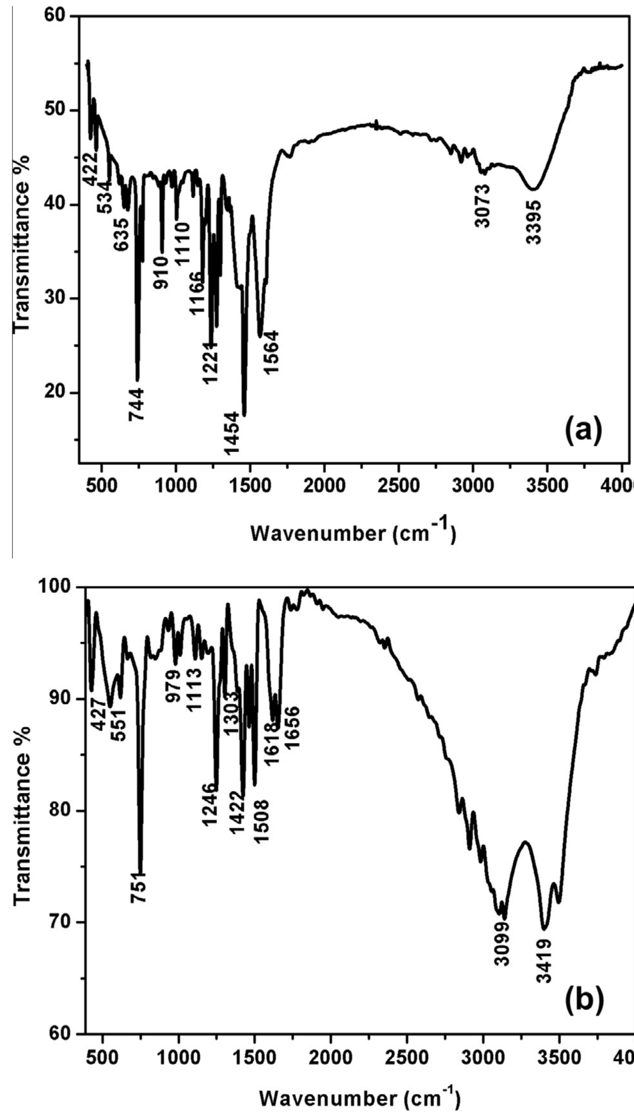

Fig. 2. FTIR spectrum of (a) Co-BMZ and (b) Cu-BMZ.

The deposited films were subjected to various characterization studies. Thickness of the samples was determined by simple optical technique [18]. The thickness of Co-BMZ thin films is ~650 nm and that of Cu-BMZ thin films is ~450 nm. Thickness of the thin films decreases with increase in the annealing temperature. The FT-IR spectra were recorded using Perkin Elmer Spectrum RX I system for powders scratched from the deposited films in the range between 400 and 4000 cm^{-1} using KBr pellet technique. Raman spectra of the films were recorded in the range between 200 and 1500 cm^{-1} using Renishaw inVia Reex Raman spectrometer in backscattering geometry. 514.5 nm Ar^+ laser was used as the source and the laser spot size is about 5 μm. The crystallinity of the samples was analysed using XPERT-PRO diffractometer system and the X-ray diffraction pattern of all the samples reveals a broad amorphous hump and no Bragg diffraction peaks were obtained. The pattern is similar to that of a typical amorphous material [19]. Surface morphology of the deposited films were analysed by Atomic Force Microscope (AFM) using SEIKO SPA400-SPI4000 AFM unit in dynamic scanning mode with a scan speed of 0.5 Hz and the radius of the tip is about 10 nm. Transmission spectra of the samples were measured using Perkin Elmer Lambda 35 UV–