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# Room temperature diluted magnetism in Li, Na and K co-doped ZnO synthesized by solution combustion method

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ABSTRACT

In this effort the alkali dopants Li, Na and K are co-doped with ZnO by solution combustion technique. This work is the production of room temperature ferromagnetism along with a rare orange emission from ZnO with equally concentrated Li, Na and K impurities. The XRD analysis reveals the hexagonal wurtzite structure and the substitution of the alkali in ZnO. The SEM and EDAX study shows the morphology and impurity free samples of ZnAO. The interstitial Zn atoms and the strain produced in the crystal structure due to alkali dopants is reflected in the FT Raman spectra. The band gap determined from the UV-Vis-NIR shows a variation that follows the variation of the grain size. The PL emission spectra brings to limelight the abundance of interstitial O atoms that involves in orange emission. The oxygen vacancies in the sample produce a weak green emission that decreases and then increases with alkali content. There is also a weak UV emission due to bound acceptor–donor recombination. The magnetometry establishes the fact that the direct bandgap semiconductor ZnO becomes magnetically sensitive due to the presence of alkali thereby making ZnO:Li + Na + K as a member of the family of dilute magnetic semiconductors. To the best of our knowledge this is the first report on the ferromagnetism observed in Li, Na and K co-doped ZnO.



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## 1. Introduction

Zinc oxide is a material with boundless potential for a countless of real-world applications like devices based on spin transport properties such as spin-light emitting diode, optical isolators, optical switches with interesting properties such as UV and visible photoluminescence and room temperature ferromagnetism [1–3]. The optical properties and magnetic properties of ZnO have been extensively studied [4–8]. The room-temperature PL spectra of ZnO typically consist of a UV emission and possibly one or more visible bands due to defects and/or impurities. There are still a number of unanswered questions concerning the relationship between fabrication conditions and the optical properties. On the other hand realizing magnetic ordering in ZnO is also considered to be a fruitful matter. ZnO shows ferromagnetic behavior depending upon the defects that may be intrinsic or extrinsic defects such as the dopants from 3d transition group or combination of a rare earth and 3d group or even from alkali group [9,10]. ZnO has been doped with alkali metals or codoped with alkali metals and rare earth impurities to see the effect in optical, conducting and magnetic properties. There are reports on ZnO:Li, ZnO:Na, ZnO:K and ZnO codoped with alkali and rare earth elements [11,12]. ZnO is synthesized by variety of techniques like such as thermal evaporation, metal–organic vapor phase epitaxy, laser ablation, hydrothermal synthesis, template-based synthesis and combustion synthesis [13–17]. Previously we have observed the ability of Na to tune the optical band gap of ZnO nanopowders [18]. We have recently reported the effect of Li in ZnO to strongly intensity the visible emission [19]. In the present work the alkali elements lithium, sodium and potassium are codoped with ZnO with a view to investigate the effects on the optical properties and magnetic properties. The synthesis is carried out by solution combustion method.

## 2. Materials and methods

ZnO:Li + Na + K powder samples (ZnAO) of three different concentrations (Li, Na, K = 1%, 2% and 3%) are synthesized by dissolving the stoichiometric amounts of zinc nitrate, lithium nitrate, sodium nitrate, potassium nitrate and glycine in distilled water to get an aqueous solution. The glycine acts as fuel for the reaction. The solution was continuously stirred and heated and this leads to a self-propagating combustion process leaving fine powders of ZnAO ultimately. The powders are heated to 500 °C and ground well and then preserved for studies. The powders are characterized by using an X-ray diffractometer (XRD) (PAnalytical X'pert PRO) and scanning electron microscope (SEM) (Bruker) for the structural properties. The optical properties are studied using Ultraviolet-Visible-Near Infra-Red spectrophotometer (UV-Vis-NIR) (LabIndia UV 3000 +), Fourier Transform Infra-Red spectrophotometer (FTIR) (Bruker Alpha-T), FT Raman spectrometer (Bruker RFS127), spectroflourimeter (JY Fluorolog-3-11) and Vibrating sample magnetometer (Lakeshore VSM 7410). All the characterizations have been performed in room temperature.

## 3. Results and discussion

### 3.1. Structural analysis

#### 3.1.1. XRD analysis

The structural properties of the samples of ZnO and ZnAO are analyzed from the XRD patterns shown in Fig. 1. The XRD patterns reveals the wurtzite structure with the standard peaks of ZnO (JCPDS 36-1451) indexed as (100), (002), (101), (102), (110), (103), (200), (112) and (201). The XRD patterns show no secondary or any other additional peaks for doped ZnO indicating the proper incorporation of alkali ions. The average crystallite sizes are determined from the XRD pattern using Debye–Scherrer relation given by:

$$G = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$