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The study of optical and colossal dielectric properties of (Cu, Ga)-doped ZnO nanoparticles

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Abstract

In this work, we have studied optical and dielectric properties of (Ga, Cu)-doped ZnO nanoparticles in both theoretical and experimental aspects. In an experimental approach, we have synthesized ZnO, Ga-doped ZnO, Cu-doped ZnO, and (Ga, Cu)-codoped ZnO nanopowder by using combustion method, then calcined nanoparticles were investigated by XRD, SEM, TEM, and UV-vis spectroscopy techniques. In the case of the first-principles calculation, 2×2×2 supercell of ZnO and (Ga, Cu)-co-doped ZnO is modeled. These systems consist of 32 atoms while two-Zn atoms are removed and replaced by Ga and Cu. Thus, it is 12.5% mole (Ga, Cu)-co-doped ZnO, same doping percentage to experiment part. In the study, density functional theory (DFT) study is conducted on VASP using GGA with Hubbard parameter (GGA+U). The supercells are firstly optimized. Then, the study carries on by density of states, and band structures calculation. To summarize, we have successfully fabricated (Ga, Cu)-co-doped ZnO nanoparticles with the particle size of 40 – 50 nm, then, optical, and dielectric properties of Ga and Cu doping on ZnO are studied. From the explored results, it can be concluded that this work successes in enhancement dielectric properties and optical properties of ZnO by Ga and Cu doping. As a result, ZnO could be a higher efficiency dielectric material and photocatalyst under Sun irradiation when it is doped by Ga and Cu ions.

Keywords: Optical properties, Colossal dielectric properties, DFT, (Cu, Ga)-codoped ZnO

1. Introduction

For more than two decades, metal oxides with high dielectric permittivity or colossal dielectric oxides have been extensively investigated because they are potentially valuable for multilayer ceramic capacitors (MLCCs). Therefore, the intriguing electric permittivity of the colossal dielectric material has strongly attracted research attention. ZnO attracts a great deal of attention since it is a semiconductor that could be applied in various applications, such as sensors, photocatalysts, optoelectronic devices [1-5]. To enhance the efficiency of ZnO properties, doping is the most favorable method [6-12]. Codoping also increases the photocatalytic activity of the photocatalysts. Among the doping atoms, Cu, Ga, and Al were studied more because, among promising dopants, they are known as preferable dopants due to their advanced attributes such as low toxicity and source abundance. Moreover, the electronic structure and atomic size of those atoms of Cu, Ga, and Al are similar. A thin film of p-type (Cu, Ga)-codoping ZnO was fabricated by a radio frequency magnetron sputtering technique, and it was found that the energy bandgap is reduced, and the carrier concentration is slightly changed. With the optimized carrier concentration, the photoelectrochemical cell (PEC) response is significantly increased [3, 4]. The crystallinity of (Ga, N)-codoped ZnO film is greatly improved comparing with N-doped ZnO, leading to significantly higher photocurrents [5]. The conductivity and optical properties of (Cu, Al)-codoped ZnO was theoretically investigated by using density functional theory (DFT) and it is found that codoping is enhancing the electronic conductivity more than single-doping, and the effect of the content of Al on the conductivity is more than that of Cu. Furthermore, the absorption of (Cu, Al)-codoped ZnO has a large red-shift due to reducing of the energy bandgap [12]. Cu doping shifts the absorption onset to blue from 373 to 350 nm, indicating an increase in the bandgap from 3.33 to 3.55 eV. A relative increase in the intensity of the deep trap emission of Cu-doped ZnO is observed when increasing the concentration of Cu, and copper ions were well incorporated into the ZnO lattices by substituting Zn sites without changing the wurtzite structure and no secondary phase existed in Cu-doped ZnO nanoparticles. According to other works, we can enhance the properties of ZnO. Therefore, in this work, we focus on optical, and dielectric properties improvement of ZnO by Ga and Cu doping. Here both theoretical and experimental aspects of Ga and Cu doped ZnO are studied.

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2. Materials and methods

2.1 Synthesis details

By using a combustion method, the ZnO, $Zn_{1-x}Cu_xO$, $Zn_{1-x}Ga_xO$ and $Zn_{1-2x}Cu_xGa_xO$ (x = 0.0625) nanopowder was prepared. $C_4H_6O_4Zn$ (Sigma-Aldrich), $Cu(NO_3)_2{\cdot}3H_2O$ (RPE-For analysis), $Ga(NO_3)3{\cdot}xH_2O$ (Sigma-Aldrich, 99.9%), NH_2CH_2COOH (ACI Labscan), DI water, and citric acid were used as the starting chemicals. For all co-doping conditions (x), the starting chemicals were mixed for each chemical formula. Firstly, $Ga(NO_3)3{\cdot}xH_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ were dissolved in deionized (DI) water with constant stirring at room temperature (RT) and a $C_4H_6O_4Zn$ was added into the solution. For Ga-doped ZnO, $GaN_3O_9.xH_2O$ was used, or $CuN_3O_9.9H_2O$ solution was mixed for the case of $Zn_{1-x}Cu_xO$ and, $GaN_3O_9.xH_2O$ and $CuN_3O_9.9H_2O$ were mixed for the $Zn_{1-2x}Cu_xGa_xO$. Then, citric acid solution and glycine solution were added. After that, the final solution was still stirred at 130 °C until a viscous gel was obtained. After the transformation to the gel of the solution, the combustion process was adopted by heating the obtained gel in the oven at 350 °C for an hour. Finally, the powder was obtained. Then, the precursor was calcined at 450 °C in the atmosphere for 5-hour with a heating rate of 5 °C/minute. Then, the calcined powders were shaped into pellets with dimensions of 9.5 mm in diameter and ~1.3 mm in thickness by uniaxial compression at 10 MPa. Finally, the pellets were sintered at 1020 °C for 5h with a heating rate of 5 °C/min, and followed by natural furnace cooling to room temperature (RT).

2.2 Characterizations

The calcined powders were characterized by using x-ray diffraction technique (XRD), scanning electron microscopes (SEM), and transmission electron microscopy (TEM). Furthermore, the optical bandgap properties of samples were studied by using UV-Vis spectroscopy. Lastly, it was hot-pressed as bulk and then polished. Then, colossal dielectric properties of synthesized samples were studied. The dielectric parameters were measured by a KEYSIGHT E4990A Impedance Analyzer in the frequency ranges of 40-10^7 Hz at room temperature.

2.3 Computational details

A unit cell of four-atom ZnO is eight-time extended as 2x2x2 supercell size. Thus, the undoped ZnO structure contains thirty-two atoms in total, 16 Zn atoms and 16 oxygen of atoms, as illustrated in Figure 1(a). For the doped ZnO structures, an atom Zn was substituted by Cu and Ga atoms for Cu-doped ZnO and Ga-doped ZnO, respectively. In co-doping, two sites of Zn are replaced by Cu and Ga, named as (Ga, Cu)-co-doped ZnO. All doped ZnO structures are shown Figure 1(b-d). The DFT calculation is performed under Vienna Ab initio Simulation Package (VASP) with Projector-augmented plane-wave pseudopotential method (PAW) [13, 14] on the generalized gradient approximation (GGA) on the schema of the Perdew–Burke–Ernzerh (PBE). Additionally, Cutoff energy of 400 eV and 21×21×21 k-point meshes in Monkhorst–Pack k-point are also employed. Electrons in Zn(d^{10} p^2), O(s^2 p^4), Cu(d^{10} p^1) and Ga(s^2 p^1) orbitals are considered as valence electrons in the study.

To summary, in the experiment, ZnO, Ga-doped ZnO, Cu-doped ZnO, and (Ga, Cu)-co-doped ZnO nanoparticles are prepared, then prepared powder is characterized by XRD, SEM, TEM, and UV-vis spectroscopy. After that, dielectric properties are measurement to explore the effect of Ga and Cu doping on ZnO. For the first-principles calculation, 2×2×2 supercell of ZnO and (Ga, Cu)-co-doped ZnO is modeled. These systems consist of 32 atoms while two-Zn atoms are removed and replaced by Ga and Cu. Thus, it is 12.5% mole (Ga, Cu)-co-doped ZnO, same doping percentage to experiment part. In the study, density functional theory (DFT) study is conducted on VASP using GGA with Hubbard parameter (GGA+U). The supercells are firstly optimized. Then, the study carries on by density of states.

3. Results

The simulated ZnO, Cu-doped ZnO, Ga-doped ZnO, and (Cu, Ga)-co-doped ZnO for this study are shown in Figure 1.

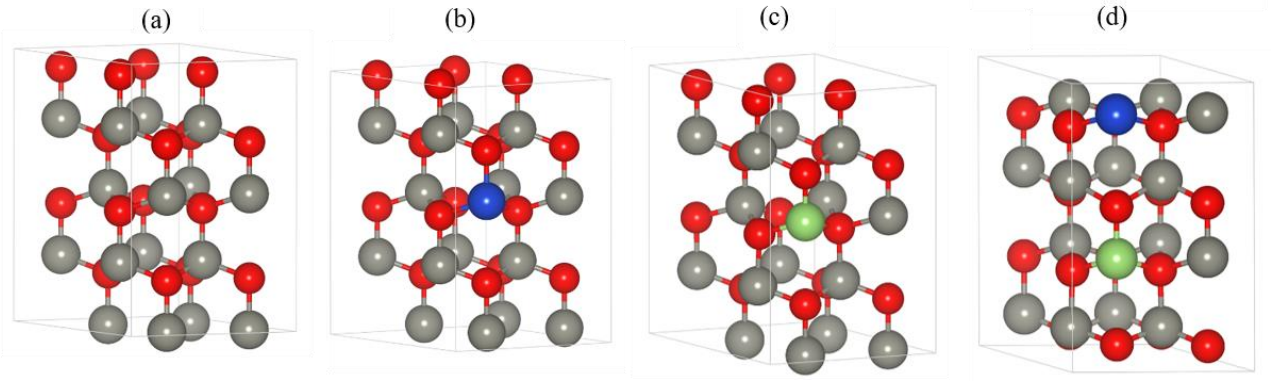

Figure 1 (a) ZnO, (b) Cu-doped ZnO, (c) Ga-doped ZnO and (d) (Cu, Ga)-co doped ZnO. Gray, red, blue, and green balls represent Zn, O, Cu and Ga atoms, respectively.

In the experimental part, the ZnO, doped and co-doped ZnO was prepared and characterized by XRD. All the samples are hexagonal wurtzite structures, as shown in Figure 2. According to XRD patterns, we used Debye-Sherrer's equation to compute the average crystallite size (D),

$$D = \frac{\kappa\lambda}{\beta\cos\theta} \quad (1)$$

where D is the average crystallite size, κ is the shape factor, λ is the wavelength of the incident x-ray beam, β is the full width at the half maximum. The average crystallite sizes were found to be about 50 nm as shown in Table 1. Furthermore, the lattice parameters of hexagonal wurtzite ZnO are calculated as,

$$\frac{1}{d^2} = \frac{4}{3(h^2 + hk + k^2/a^2)} + \frac{l}{c^2} \quad (2)$$

where a and c are the lattice parameters, h, k and l are the miller indices and d is the interplanar spacing, computed from,

$$2dsin\theta = n\lambda \quad (3)$$

Table 1 Lattice constants and average crystallite sizes of ZnO and doped ZnO

Sample	Lattice parameter (A)		Average crystallite sizes (A)
	a	***c***	
ZnO	3.25087	5.20782	437.778
6.25%Cu-ZnO	3.25117	5.20814	338.375
12.5%Cu-ZnO	3.25125	5.20767	400.220
6.25%Ga-ZnO	3.25272	5.20614	510.556
(Ga+Cu)-ZnO	3.25228	5.20397	501.889

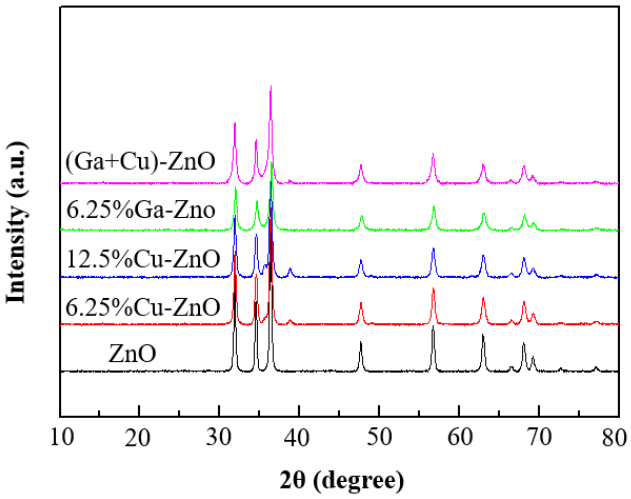

Figure 2 XRD Patterns of the calcined samples.

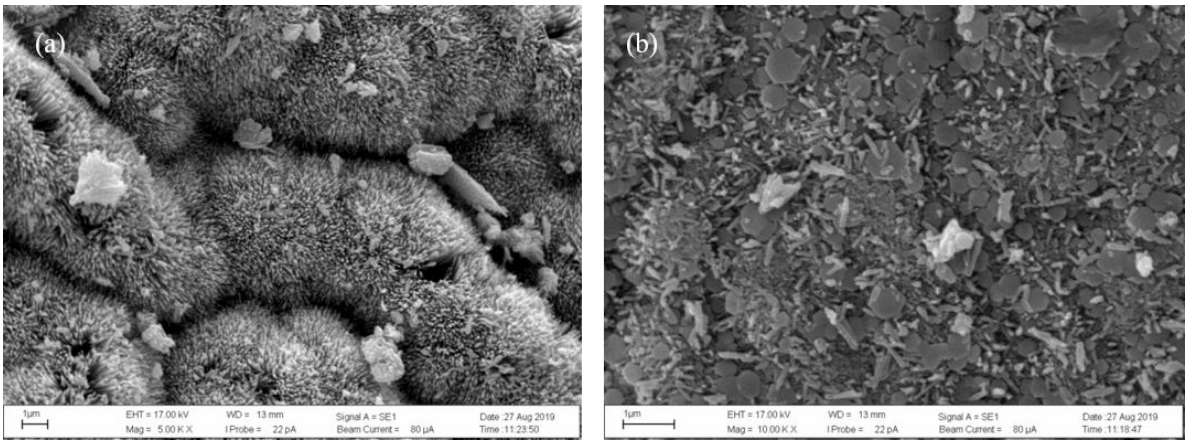

Figure 3 SEM Images of (a) Ga-doped ZnO and (b) undoped ZnO.

The morphology of calcined samples was investigated using SEM and TEM techniques. The SEM images of the synthesized were shown in Figure 3. Morphology of all samples is nanoparticles of hexagonal structure. When doped elements were added into zinc oxide structure, particle shape converts from hexagonal to spike-like shape and nanowires. Moreover, doping of Cu and Ga into the ZnO, nanoparticles, as shown in Figure 4 or TEM images, it is clear that particle size changes from hexagonal with an average around 40-50 nm to more spherical with an average around 20-40 nm, after doping the Cu and Ga content.

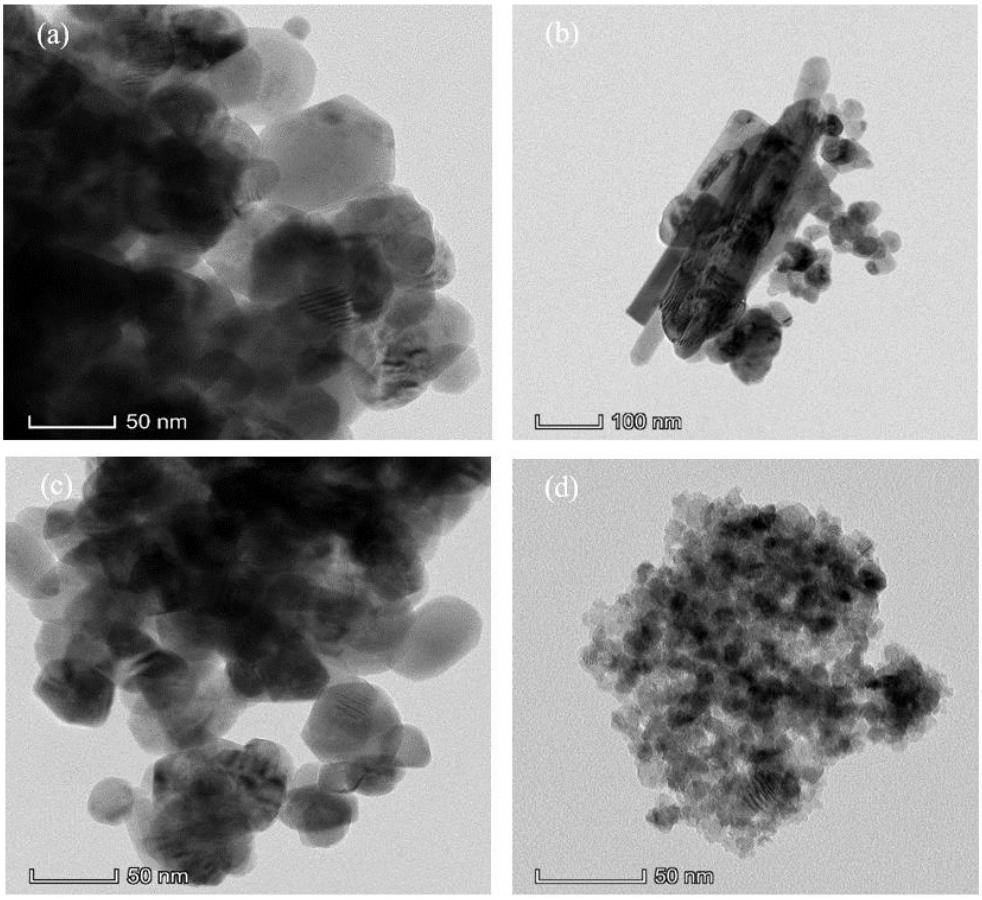

Figure 4 TEM Images of (a) undoped ZnO, (b) Ga-doped ZnO, (c) Cu-doped ZnO and (d) (Cu, Ga)-co doped ZnO.

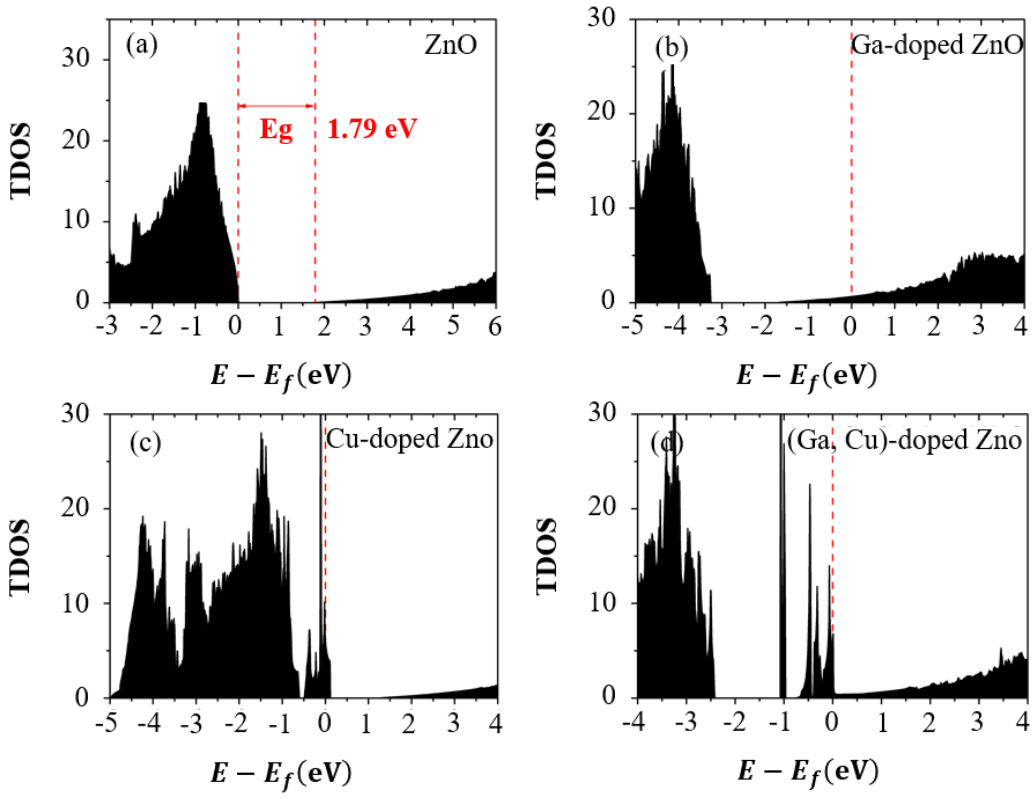

Figure 5 Total density of states of (a) pure, (b) Ga-doped, (c) Cu-doped, and (d) (Ga, Cu)-doped ZnO.

For the calculation part, the total DOS of optimized structures of ZnO and (Cu, Ga)-doped ZnO, as shown in Figure 5, were studied. For pure ZnO, the topmost filled state is occupied by d-orbital electrons of Zn and p-orbital electrons of O. The calculated energy gap

is 1.76 eV which is underestimated compared to the experiment value, due to the general disadvantage of the DFT. When Cu and Ga atoms are added into the ZnO structure, there are new states observed above the valence band maximum and the fermi level was the move to the conduction band. Therefore, it infers that new states in the conduction band could increase their electronic conductivity [15-20]. For Cu-doped ZnO, there are intermediate states appear between the valence band and conduction band, and doping with Ga causes shifting the Fermi level in the conduction band, leading to increase electronic conductivity. According to this, adding Cu and Ga in ZnO can be used to engineer DOS of ZnO, which might lead to beneficial optical and dielectric properties.

The energy band gaps of the ZnO, Cu-doped ZnO, Ga-doped ZnO, and (Cu, Ga)-codoped ZnO can be determined by using the equation,

$$\alpha h\nu = k(h\nu - E_g)^{n/2} \quad (4)$$

where α is the absorption coefficient, h the Plank's constant and ν the photon frequency k and n are constants, and n should be 1 and 4 for direct and indirect bandgap materials. According to Figure 6, the graphs show the energy bandgap (E_g) of 3.05 eV, 2.93, 2.91, and 3.01 eV for ZnO, Ga-doped ZnO, Cu-doped ZnO, and (Cu, Ga)-co-doped ZnO, respectively.

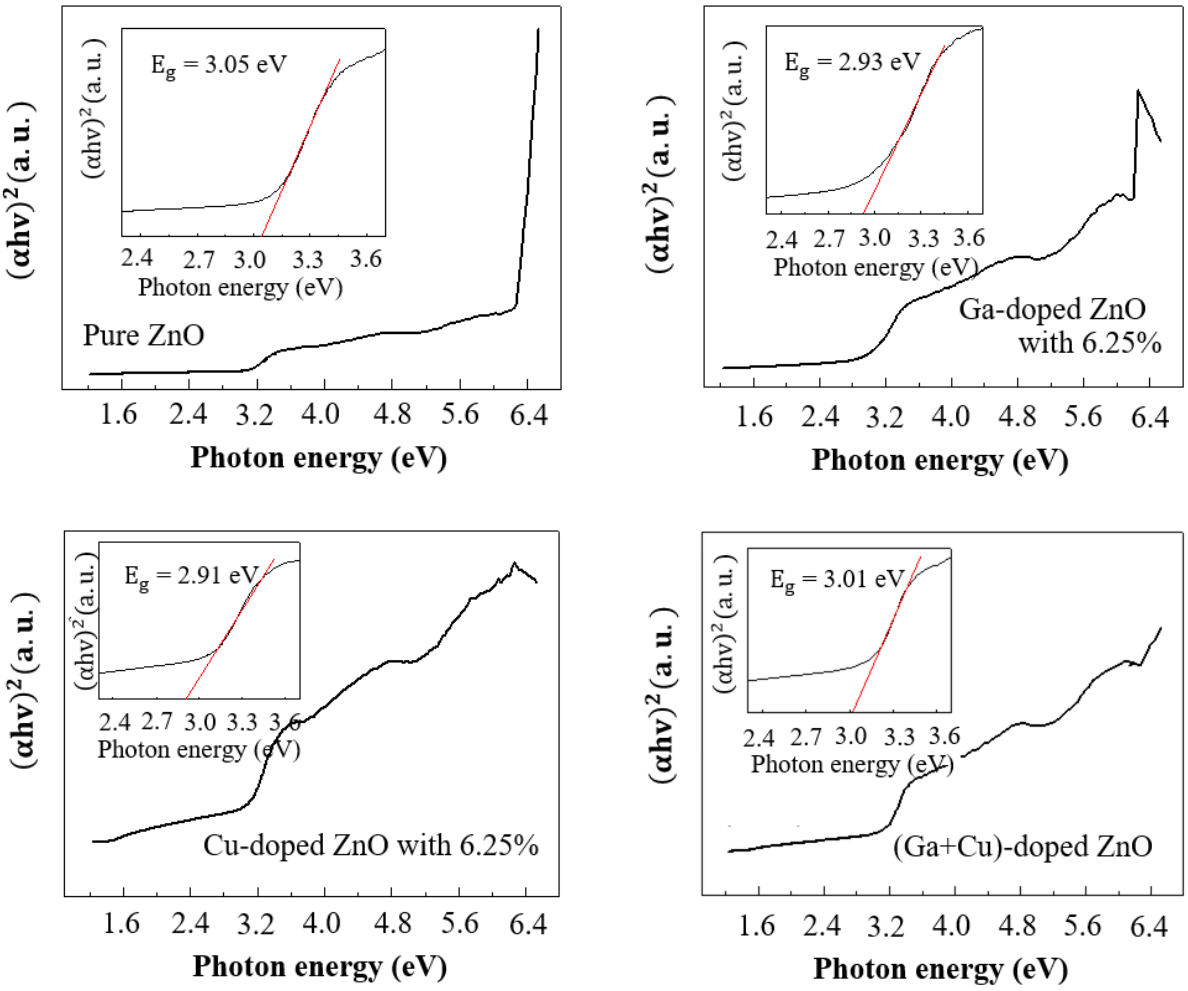

Figure 6 Graphs of $(\alpha h\nu)^{1/2}$ versus photon energy of undoped ZnO and (Ga, Cu)-doped ZnO.

Table 2 Dielectric permittivity and loss tangent of ZnO and doped ZnO at the frequency of 1 kHz

Sample	ε'	$tan\delta$
ZnO	1,175.65	3.953
6.25% Cu-doped ZnO	43.75	3.833
12.5 Cu-doped ZnO	33.73	1.147
6.25% Ga-doped ZnO	119,246.35	0.873
6.25% (Cu, Ga)-codoped ZnO	1892.90	11.559

Now turning into the colossal dielectric properties, the dielectric properties of ZnO ceramics at room temperature are shown in Figure 7. In the frequency range below 10^4 Hz, very high values of ε′ were obtained in all sintered ceramics for Ga-doped and (Cu, Ga)-codoped ZnO. Especially for Ga-doped ZnO ceramics, it shows very good giant dielectric property, i.e high dielectric constant (around 120,000) and low tanδ (around 0.88), as shown in the Table 2. This result suggested that single doping, and co-doping ions, especially Ga doping, have played an important role in the dielectric response of ZnO ceramics.

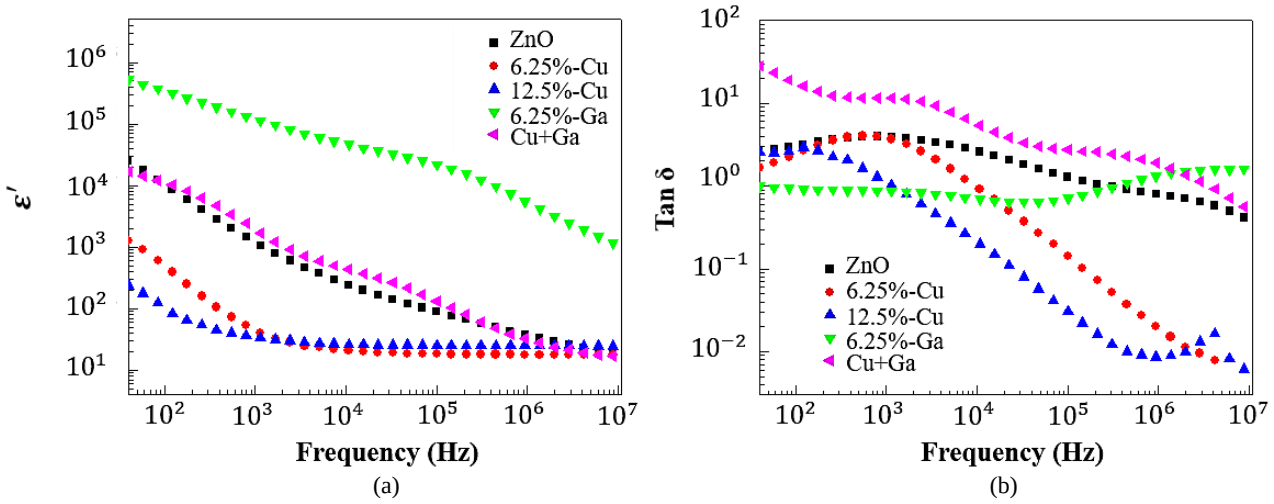

Figure 7 (a) Dielectric permittivity and (b) loss tangent of undoped ZnO, single-doped, and (Ga, Cu) co-doped ZnO.

4. Discussion

From the study, Ga and Cu doping ions affect band gap energy (E_g), dielectric permittivity (ε'), loss tangent ($tan\delta$), and magnetic behavior. First, E_g is smaller when Ga and Cu are co-doped on ZnO, changing from 3.05 eV to 3.01 eV when ZnO is co-doped by Ga and Cu, as shown in Figure 6. This result has corresponded to DFT calculation. As shown in Figure 5, the total density of states of ZnO is changed when ZnO is co-substituted by Ga and Cu ions. Being smaller than E_g is expected to absorb more Sunlight, leading to higher photocatalysis performance under Sun irradiation. Moreover, ε' is greatly larger after ZnO was doped by Ga. The ε' value at 1 kHz of ZnO is 1,175.65, while ε' slightly increases as 1,892.90 when ZnO is codoped by Ga and Cu. Then, ε' reaches the maximum value of 119,246.35 when ZnO is doped by Ga, as illustrated in Figure 7(a). It is more than 100 times of undoped ZnO. Additionally, the loss tangent also changes, and the graph is shown in Figure 3(b). $tan\delta$ changes from 3.953 to 0.873 for ZnO and Ga-doped ZnO, respectively. Interestingly, the dielectric properties of ZnO can be greatly improved by the substitution of Ga ion. Therefore, Ga doping ion greatly affects the dielectric properties of ZnO. From these results, it is shown that valence electrons of Ga and Cu can play an important role in the optical, and dielectric properties of ZnO. Ga and Cu doping can improve dielectric properties and engineer the energy bandgap of ZnO [21, 22].

5. Conclusions

To summarize, we have successfully fabricated (Ga, Cu)-co-doped ZnO nanoparticles with the particle size of 40 – 50 nm, then, optical, and dielectric properties of Ga and Cu doping on ZnO are studied. From the explored results, it can be concluded that this work successes in enhancement dielectric properties and optical properties of ZnO by Ga and Cu doping. As a result, ZnO could be a higher efficiency dielectric material and photocatalyst under Sun irradiation when it is doped by Ga and Cu ions.

6. Acknowledgements

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7. References

[1] Sikam P, Sararat C, Moontragoon P, Kaewmaraya T, Maensiri S. Enhanced thermoelectric properties of N-doped ZnO and $SrTiO_3$: a first-principles study. Appl Surf Sci. 2018;446:47-58.
[2] Sikam P, Moontragoon P, Ikonic Z, Kaewmaraya T, Thongbai P. The study of structural, morphological and optical properties of (Al, Ga)-doped ZnO: DFT and experimental approaches. Appl Surf Sci. 2019;480:621-35.
[3] Shet S. (Ga,N) and (Cu,Ga) Co-Doped ZnO Films for improving photoelectrochemical response for solar driven hydrogen production. ECS Trans. 2010;33(26):95.
[4] Shet S, Ahn K, Yan Y, Deutsch T, Chrustowski KM, Turner JT, et al. Carrier concentration tuning of bandgap-reduced p-type ZnO films by codoping of Cu and Ga for improving photoelectrochemical response. J Appl Phys. 2008;103(7):073504-5.
[5] Sikam P, Thirayatorn R, Moontragoon P, Kaewmaraya T, Amornkitbamrung V, Ikonic Z. The quantum confined stark effect in N-doped ZnO/ZnO/N-doped ZnO nanostructures for infrared and terahertz applications. Nanotechnology. 2020;31(44):445207.
[6] Roguai S, Djelloul A. A structural and optical properties of Cu-doped ZnO films prepared by spray pyrolysis. Appl Phys. 2020;126(2):122.
[7] Saad LB, Soltane L, Sediri F. Pure and Cu-Doped ZnO nanoparticles: hydrothermal synthesis, structural, and optical properties. Russ J Phys Chem. 2019;93:2782-8.
[8] Xie J, Guo C, Li CM. Ga doping to significantly improve the performance of all-electrochemically fabricated Cu_2O-ZnO nanowire solar cells. Phys Chem Chem Phys. 2013;15(38):15905-11.

[9] Gong L, Lu J, Ye Z. Conductive Ga doped ZnO/Cu/Ga doped ZnO thin films prepared by magnetron sputtering at room temperature for flexible electronics. Thin Solid Films. 2011;519(11):3870-4.
[10] Farha AH, Ibrahim MM, Mansour SA. Ga-doped ZnO nanostructured powder for cool-nanopigment in environment applications. Mater. 2020;13(22):1-16.
[11] Ponja SD, Sathasivam S, Parkin IP, Carmalt CJ. Highly conductive and transparent gallium doped zinc oxide thin films via chemical vapor deposition. Sci Rep. 2020;10(1):638.
[12] Ma Z, Ren F, Ming X, Long Y, Volinsky AA. Cu-Doped ZnO electronic structure and optical properties studied by first-principles calculations and experiments. Mater. 2019;12(1):196.
[13] Kresse G, Furthmuller J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput Mater Sci. 1996;6(1):15-50.
[14] Blochl PE. Projector augmented-wave method. Phys Rev B. 1994;50(24):17953-79.
[15] Dai J, Suo Z, Li Z, Gao S. Effect of Cu/Al doping on electronic structure and optical properties of ZnO. Results Phys. 2019;15:102649.
[16] Hammad TM, Salem JK, Harrison RG. Optical and magnetic properties of Cu-doped ZnO nanoparticles. J Mater Sci Mater Electron. 2013;24:2846-52.
[17] Hou DL, Ye XJ, Meng HJ, Zhou HJ, Li XL, Zhen CM, et al. Magnetic properties of n-type Cu-doped ZnO thin films. Appl Phys Lett. 2007;90:142502.
[18] Jantrasee S, Pinitsoontorn S, Moontragoon P. First-principles study of the electronic structure and thermoelectric properties of al-doped ZnO. J Electron Mater. 2014;43(6):1689-96.
[19] Jantrasee S, Moontragoon P, Pinitsoontorn S. Optical and magnetic properties of doped ZnO: experi-mental and simulation. J Optoelectron Adv Mat. 2016;18(11-12):1033-9.
[20] Jantrasee S, Moontragoon P, Pinitsoontorn S. Thermoelectric properties of Al-doped ZnO: experiment and simulation. J Semicond. 2016;37(9):092002.
[21] Liu H, Yang J, Hua Z, Zhang Y, Yang L, Xiao L, et al. The structure and magnetic properties of Cu-doped ZnO prepared by sol-gel method. Appl Surf Sci. 2010;256:4162-5.
[22] Jang C, Jiang Q, Lu J, Ye Z. Structural, optical and electrical properties of Ga doped ZnO/Cu grid/Ga doped ZnO transparent electrodes. J Mater Sci Tech. 2015;31:1108-10.