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Optical and Electrical Properties of Transition Metal Ion doped Sol-Gel Materials

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Introduction

Bright inorganic powders are of high technological interest because of their potential applications in diverse areas such as electronics, where they can be used in opt-electronic devices, i.e. laser diodes and light emitting diodes, optical-fibres and optical-fibre amplifiers. There are uses in electrochemistry and catalysis, as well as industrial applications in aircraft. Their emission can cover a wide range of frequencies [1-4] and their visible colouration originates from the presence of a transition metal ion and ligand field effects. This relates mainly to the presence of inter valence charge-transfer between the transition metal and in inorganic host materials. Powders such as zinc silicates can be processed by solid state methods that lead to agglomerated particles several μm in size. Employing a low energy process such as sol-gel, forced precipitation, organometallic complex route, combustion methods, dry reaction, spray-pyrolysis, pulsed laser deposition (PLD), polymer assisted methods, etc., can help to overcome the limitations of solid-diffusion [5,6]. A very effective method that can be used to control the morphology is the sol-gel method. Sol-gel requires lower processing temperature and employs the use of solvents such as water, alcohol or ionic liquid. Zinc nitrate, sulphate, chloride or acetate as well as silica, silicates and alkoxysilanes can be used as the starting materials. In the sol-gel method, materials that are dissolved or dispersed in solvents are then mixed to produce a homogeneous solution or uniform dispersion. These homogeneous solutions or dispersions can be coated onto a substrate or simply dried and as such, the sol-gel method provides a uniform composition [6-9].

Practically, full-colour display devices that use the zinc silicate family of compounds as the phosphor provide for simple luminescence and processing, since these materials have similar densities, surface potentials, and conductivities [10-12]. Zinc silicates have a promising future as advanced materials as they are highly versatile luminescence materials. They enable a wide range of multi-colour emitting phosphors to be produced compared to the visible light region, with the colour dependent on the choice of the doping ion [13-15]. Sol-gel methods are similar to solid-state reactions from the standpoint of producing α -phase Zn₂SiO₄. Traditionally, the solid state diffusion method has been employed for the synthesis of Zn₂SiO₄, which involves crushing, grinding, ball milling, and sintering of source materials at very high temperatures, whereas the phase formation of Zn₂SiO₄ for most sol-gel methods needs calcinations at lower temperatures (around 800°C). During sol-gel processing, particle size and morphology can be well controlled [14]. Therefore, Sol-gel methods can be ideal for the production of the above materials.

Research into the development of new coloured inorganic solids based on transition metal ions in unusual oxidation states or in unusual irregular coordination geometries, have led to the investigation of forming coloured materials by doping 3d metal ions such as Mn^{2+} , Co^{2+} , Ni^{2+} in a novel host such as Zn_2SiO_4 , Mg_2SiO_4 , Mg_2TiO_4 [13-15]. It is thought that doping divalent 3d metal ions at the Zn(II) site can give rise to novel coloured materials that could reflect the distorted octahedral/ fivefold coordination geometry of Zn(II) in the host. Much research on colour generation and luminescent behaviour of Cr^{3+} ions in glasses and single crystals have been examined in terms of the transition metal coordination number. These results are often interpreted based on the ligand field theory [16]. It is well known, that Cr^{3+} ions preferentially occupy octahedral sites in glasses and crystals, as indicated by their large site stabilizing energy [15-17]. The colour and the positions of the absorption bands change depending on the ligand field parameters. Many new optical applications and systems that use Zn_2SiO_4 : Mn^{2+} and Zn_2SiO_4 have been aimed at exploiting their convenient properties and chemical stability. For example, an inverse opal photonic crystal consisting of Zn_2SiO_4 : Mn^{2+} was proposed as a light source for a display device [18, 19]. In addition, cobalt (II) and nickel (II) ions are known to be good probes for optical

absorption studies. Applications for a blue pigment have been intensively explored by adding Co^{2+} ions to exploit the chemical stability of the Zn_2SiO_4 structure [20]. The microwave dielectric properties of Zn_2SiO_4 have been beneficial for its use as a substrate material for microwave-integrated circuits [21-24].

Chandra Babu and Buddhudu investigated Zn_2SiO_4 as a host material [25] and found that when rare earth ions (Tb^{3+} , Eu^{3+} and Ce^{3+}) were added to this sol-gel powder, a strong interaction between the host and the dopant were observed, which was apparent by more intense emission and absorption bands. When Li⁺ for example was co-doped along with rare earth ions, more encouraging and significant enhanced emission results were obtained when compared to the absence of a co-doped ion [26, 27]. By noticing these important trends, rare earths in those matrices can be considered as dopant luminescent ions and it is our intent in this work to investigate the spectral properties of willemite α -Zn₂SiO₄ by adding five different transition metal (Cr^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} & Cu^{2+}) ions separately and to understand their optical and dielectric properties.

The aim of this chapter is to review the optical and dielectric properties of the transition metal $(TM^{2+/3+})$ doped $Cr^{3+}:Zn_2SiO_4$, $Mn^{2+}:Zn_2SiO_4$, $Co^{2+}:Zn_2SiO_4$, $Ni^{2+}:Zn_2SiO_4$ and $Cu^{2+}:Zn_2SiO_4$ powders synthesized by a sol-gel method.

Characterisation of TM^{2+/3+} doped Zn₂SiO₄ powders

Chemical Composition and XRD Analysis

In order to verify the presence of Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺ and Cr³⁺ ions in the doped powders, the Energy-dispersive X-ray analysis (EDAX) profiles were recorded. **Figure 9.1** (a, b, c, d & e) shows the profiles of Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺ and Cr³⁺ doped Zn₂SiO₄ sol-gel derived powders respectively, with each sample sintered at 1000 °C for 2 h. From the EDAX profile, it is obvious that the final product contains a high atomic percentage of Zn and Si, as compared to the small doping concentrations of the TM ions. No traces of other elements were noticed in these profiles, thus confirming the purity of the samples with near stoichiometry.Zn₂SiO₄ under ordinary conditions crystallizes to a rhombohedral phenacite with parallel-faced hemihedrism structure; space group $R(\overline{(3)})$ (148), with both Zn²⁺ and Si⁴⁺ ions tetrahedrally coordinated to four oxygen atoms. The room temperature XRD patterns of Zn₂SiO₄ and 0.05 mol% doped Cr³⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺: Zn₂SiO₄ sol-gel derived powders after sintering at 1000 °C for 2 h are shown in **Figure 9.2**.

The diffraction patterns show sharp, well-defined, diffraction peaks. It can be observed that all Cr^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} doped α -Zn₂SiO₄ peak positions are in agreement with the standard patterns of the Joint Committee on Powder Diffraction Standards (JCPDS, 79-2005) for Zn₂SiO₄ in a Willemite structure. No other impurity peaks could be observed in the XRD patterns, thus indicating single-phase samples. All samples exhibited main diffraction peaks related to the planes (1 1 0), (12-1) (3 0 0), (2 2 0), (1 1-3), (1 3 2), (1 4 0), (0 4 2), (0 3 3), (2 2 -3), (5 1 1), (1 2 4), (3 3 -3), (4 4 0) and (7 1 -3) that were deconvoluted to Lorentzian curves for the determination of the crystallite size using the full width at half maximum method (FWHM). The crystallites of nanocrystalline samples obtained from an XRD peak (1 3 2) planes indicate that the products possess a pure phase in rhombohedral (a=b and c with space group (148)) structure [10, 23]. The calculated crystallite size (D) of the samples was calculated using full width at half maxima (FWHM) by using Deby-Scherrer's formula [28].



FIGURE 9.1 EDAX profile of Cu²⁺, Ni²⁺, Co^{2+,} Mn²⁺& Cr³⁺: Zn₂SiO₄ powder (a, b, c, d & e)





$$D_{\text{crystallite}} = \frac{k\lambda}{\beta(2\theta)\cos\theta}$$
(1),

Where *D* was the crystallite size, k was Scherer's constant = 0.96, $\lambda = 1.5406$ Å (X-ray wavelength), and β was full width at half maxima at diffraction angle 20. *D* is the average diameter of the crystallite size. All the peaks were indexed and lattice constants (*a* and *c*) and cell volume of unit cell for each concentration were calculated by the following relations respectively [29, 30].

$$\sin^2\theta = \frac{\lambda^2}{3a^2} \left(+ hk + k^2 \right) + \left(\frac{\lambda^2}{4c^2} \right) l^2$$
(2),

Here λ is the X-ray wavelength, **a** and **c** are the lattice constants and (h k l) are the corresponding Miller indices.

(3),

$V = a^2 c \sin 120^{\circ}$

The calculated crystal size (D), the lattice parameters (a=b and c) and the cell volume ($V(Å^3)$) of all doped samples are displayed in **Table 9.1**. From the data it can be observed that the crystal size, lattice parameters and cell volume of doped Zn₂SiO₄ are similar. These results also indicate that

 Zn^{2+} ions could be replaced by Cr^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} ions in the lattice structure, because of the small difference in the ionic radii. XRD patterns of the transition metal (TM) ion doped samples are almost the same as that for the un-doped sample. No characteristic diffraction peaks of the dopant were observed because the molar ratio of TM ions in the doped samples was low. Including Cr in the doped Zn_2SiO_4 sample, the intensity of the prominent peaks at (113) and (410) decreases and slightly shifts toward lower angles. From the XRD peaks it is observed that, full width at half maximum (FWHM) increases and its intensity decreases. But there is not any change in lattice parameter; the dopant ion is small at the molecular level.

TABLE 9.1

Crystallographic parameters of rhombohedral crystal system, TMions doped Willemite α - Zn₂SiO₄ with space group R(3) (148) ceramic powders by the sol-gel method

	Parameters	d- spacing (Å)	D-crystallite	Lattice parameters (Å)		Cell Volume (V(Å ³))
Samples	(A)	5120(1111)	a=b	С		
	Zn ₂ SiO ₄	2.83370	29.80	13.923	9.303	1562
	Zn ₂ SiO ₄ :Cr ³⁺	2.84568	29.80	13.922	9.304	1562
	Zn ₂ SiO ₄ : Mn ²⁺	2.86789	29.80	13.923	9.303	1562
	Zn ₂ SiO ₄ :Co ²⁺	2.84124	29.80	13.953	9.316	1570
	Zn ₂ SiO ₄ :Ni ²⁺	2.63287	29.99	13.920	9.305	1562
	Zn ₂ SiO ₄ :Cu ²⁺	2.63411	29.99	13.926	9.309	1563

Raman Spectral Analysis

Figure 9.3 displays the Raman profiles of sol-gel derived powders for Zn_2SiO_4 and doped Zn_2SiO_4 recorded at room temperature. The spectrum of crystalline Zn_2SiO_4 possesses vibrational peaks with strong Raman scattering centred at 868 cm⁻¹, 904 cm⁻¹ and 947 cm⁻¹ originating from the siloxane group and a sharp intense peak at 472 cm⁻¹ originating from the siloxane linkage. Also, the presence of some weak signal bands can be seen at lower frequencies; $107cm^{-1}$, $221cm^{-1}$, $290cm^{-1}$ and 405 cm⁻¹ and is associated with 5-, 6-, 10- member rings present in the structure [31]. In **Table 9.2**, the Raman bands from 0 to 300 cm⁻¹ correspond to lattice vibrations, while the regions between $800 - 1100 cm^{-1}$ and $300 - 700 cm^{-1}$ can be assigned to the stretching and bending vibrations of the SiO₄ group, respectively [31, 32]. From **Figure 9.3**, it can be seen that the overall shape of the Raman spectra for the doped samples is similar, but the most intense bands; 868, 904 and 947 cm⁻¹ exhibit a small shift to lower wave numbers compared to the host Zn_2SiO_4 Raman spectrum. In the case of Mn^{2+} doped sample, it should be noted that this is a highly fluorescent material in comparison to the other TM ion doped Zn_2SiO_4 samples in this study. The small shift in the Raman bands can be due to the sub lattice producing some of the bending and stretching vibrations bonds present in the doped samples.



FIGURE 9.3

Raman profiles of Zn₂SiO₄& Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺& Cr³⁺: Zn₂SiO₄ sol-gel derived powders

TABLE 9.2

Raman band assignments

Raman bands	Assignments		
100 to 300 cm ⁻¹	lattice vibrations		
300 to 700 cm ⁻¹	bending vibrations of the SiO ₄ group		
800 to 1100 cm ⁻¹	Stretching vibrations of SiO ₄ group		
868cm ⁻¹	crystalline Zn ₂ SiO ₄ vibrational peaks		
904cm ⁻¹	(which are originated from the surface of siloxane		
947cm⁻¹	group)		

Optical analysis of Cu²⁺:Zn₂SiO₄

The absorption and emission spectra of TM ions are influenced by the nature of their host matrix. The absorption spectra of TM ions tend to be quite broad and are sensitive to the changes in coordination and symmetry. The presence of various oxidation states means that each state can give rise to different absorption spectrum, which can be explained by the application of the ligand field theory.

The optical absorption spectrum of a $Cu^{2+}:Zn_2SiO_4$ xero-gel is shown in **Figure 9.4** with two main absorption bands at 426 nm $({}^{2}B_{1g} \rightarrow {}^{2}E_{g})$ and 774 nm $({}^{2}B_{1g} \rightarrow {}^{2}B_{2g})$. It has been reported, that the absorption band near 800 nm $({}^{2}B_{1g} \rightarrow {}^{2}B_{2g})$ relates to the Cu^{2+} ion in O_h coordination with a strong tetragonal distortion [33]. The absorption band around 400 nm $({}^{2}B_{1g} \rightarrow {}^{2}E_{g})$ is the *d*-*d* transition of monovalent natured (Cu^{1+}) ions [34]. The value of crystal field strength parameter (D_q =1285 cm⁻¹), has been obtained from the profile of the optical absorption spectrum.



FIGURE 9.4

Absorption spectrum of Cu2+:Zn2SiO4 xero-gel

Figure 9.5(a) shows an excitation spectrum of 0.05 mol% Cu²⁺ doped Zn₂SiO₄ sol-gel derived powder, which was sintered at 1000 °C for 2 h. According to the ligand field theory [33] the oxide-based silicate host matrix could show charge transfer bands in UV region because of the absorption by the oxygen ligand around the cation, which normally falls in the wavelength range of 250-350 nm. Accordingly, for the 0.05 mol% Cu²⁺:Zn₂SiO₄ sol-gel derived powder, four excitation bands at 276 nm, 355 nm, 369 nm and 414 nm have been observed. The bands at 276 nm, 355 nm and 369 nm can be related to charge transfer phenomena of O²⁻ with a UV radiation exposure. **Figures 9.5(b)** and **(c)** show the emission spectra of the Cu²⁺:Zn₂SiO₄ sol-gel derived powder with excitation at 355nm and 414 nm, respectively. By using an excitation at λ_{exci} =355nm, four emission peaks at 398 nm, 456 nm, 484 nm and 584 nm were found, whereas with λ_{exci} =414 nm, three emission peaks at 455 nm, 513 nm and 564 nm were observed. These emission peaks are relatively more intense.



FIGURE 9.5

(a) Excitation, (b & c) emission spectra of Cu^{2+} : Zn_2SiO_4 sol-gel derived powder

Optical analysis of Ni²⁺:Zn₂SiO₄

The optical absorption spectrum of a Ni²⁺: Zn₂SiO₄ xero-gel, recorded at room temperature, is shown in **Figure 9.6**. The spectrum of Ni²⁺ doped Zn₂SiO₄ xero-gel exhibits five clearly resolved intense absorption bands in the visible and NIR regions; at 1238 nm (O_h1), 1160 nm (T_d1), 721 nm (O_h2), 655 nm (T_d2), 390 nm (O_h3) and a sixth weak band at 960 nm (spin forbidden). Using Tanabe-Sugano diagrams for the Ni²⁺ (d⁸) ion, the spectra have been analyzed and the bands O_h1, O_h2 and O_h3 are assigned to the transitions ${}^{3}A_{2g}$ (F) $\rightarrow {}^{3}T_{2g}$ (F), ${}^{3}A_{2g}$ (F) $\rightarrow {}^{3}T_{1g}$ (F) and ${}^{3}A_{2g}$ (F) $\rightarrow {}^{3}T_{1g}$ (P) of octahedrally positioned Ni²⁺ ions [35]. The bands in the sol-gel derived sample at 1160 nm (T_d1), and 655(T_d2) nm are attributed to the transitions ${}^{3}T_{1g}$ (F) $\rightarrow {}^{3}A_{2g}$ (F), and ${}^{3}T_{1g}$ (P) of Ni²⁺ ions in T_d sites, the band at 960 nm represents spin forbidden O_h transition of ${}^{3}A_{2g} \rightarrow {}^{1}E_{g}$ (D) [36, 37].



FIGURE 9.6 Absorption spectrum of Ni²⁺:Zn₂SiO₄ xero-gel

TABLE 9.3

Absorption spectral analysis of $TM^{3+/2+}$ ion doped Zn_2SiO_4 xero-gel glasses

	Absorption Positions (nm)	Optical absorption transitions	Crystal field parameter D _q (cm ⁻¹)	Racah parameters	
Samples				<i>B</i> (cm⁻¹)	<i>C</i> (cm ⁻¹)
Cr ³⁺ :Zn ₂ SiO ₄	412 578 682	$\label{eq:A2g} \begin{array}{l} {}^{4}A_{2g}(F) {\rightarrow} {}^{4}T_{1g}(F) \\ {}^{4}A_{2g}(F) {\rightarrow} {}^{4}T_{2g}(F) \\ {}^{4}A_{2g}\left(F\right) {\rightarrow} {}^{2}E_{g}(G) \end{array}$	1691	704	3170
Mn ²⁺ :Zn ₂ SiO ₄	444	${}^{6}A_{1g}(S) \rightarrow {}^{4}T_{1g}(G$	2252	No values	
Co ²⁺ :Zn ₂ SiO ₄	510 896 971 1179	$^{4}A_{2g}(F)$ → $^{2}T_{2g}(G)$ $^{4}A_{2g}(F)$ → $^{4}T_{1g}(F)$	405	752	3386
Ni ²⁺ :Zn ₂ SiO ₄	1238 721 390 960 (Spin forbidden)	$\frac{\text{Ni}^{2+} \text{ in } O_{h}}{{}^{3}\text{A}_{2g}(F) \rightarrow {}^{3}\text{T}_{2g}(F)}$ ${}^{3}\text{A}_{2g}(F) \rightarrow {}^{3}\text{T}_{1g}(F)$ ${}^{3}\text{A}_{2g}(F) \rightarrow {}^{3}\text{T}_{2g}(P)$ ${}^{3}\text{A}_{2g} \rightarrow {}^{1}\text{E}_{g}(D)$	742	1067	4304
	655 1160	$\frac{\text{Ni}^{2+} \text{ in } T_d}{{}^3\text{T}_{1g}(F) \rightarrow {}^3\text{A}_{2g}(F)}$ ${}^3\text{T}_{1g}(F) \rightarrow {}^3\text{T}_{1g}(P)$			
Cu ²⁺ :Zn ₂ SiO ₄	778	$^{2}B_{1g} \rightarrow ^{2}B_{2g}$	1285	No values	

Table 9.3 presents the crystal field strength D_a, and the energy level characteristics Racah B and C parameters. Accordingly, the ligand field strength $10D_a$, of Ni²⁺ in octahedral symmetry was evaluated directly from the transition energy of the ${}^{3}A_{2g}$ (F) $\rightarrow {}^{3}T_{2g}$ (F) band. The Dq, B, and C parameters were obtained by applying the wave numbers of v_1 , v_3 and v_4 bands to expressions given by solving the Tanabe-Sugano matrix [36, 37]. Generally, the ligand field strength of 3d-TM ions is related to the valency, coordination site and electron-donating properties, as those depend on the ligand anions in the materials studied. Figure 9.7(a) presents the excitation spectrum of 0.05 mol% Ni²⁺:Zn₂SiO₄ sol-gel derived powder sintered at 1000 °C for 2 h revealing two sharp excitation bands at 371 nm and 407 nm that are assigned to ${}^{3}A_{2}({}^{3}F) \rightarrow {}^{3}T_{1}({}^{3}P)$, ${}^{1}T_{2}({}^{1}D)$ transitions following a literature report [38]. Figures 9.7(b) & (c) present the emission spectra of the 0.05 mol% Ni²⁺ doped Zn₂SiO₄ sol-gel derived powder samples obtained at two different excitation wavelengths; 371nm and 407 nm, respectively. With an excitation at 371 nm, two sharp emission bands at 506 nm (blue) and 610 nm (green) are observed. When the excitation wavelength is at 467 nm, the emission spectrum exhibits three emission bands; 506 nm (blue), 555 nm (green) and 668 nm (red), respectively. The band arising at 555 nm can be assigned to the ¹T₂ - ³A₂ transition [39]. Therefore, the PL spectra of the Ni²⁺ doped samples are strongly dependent on the excitation wavelength. According to the energy level schemes, emissions in the blue, green and red regions are assigned to ${}^{3}T_{1}({}^{3}P) \rightarrow {}^{3}A_{2}({}^{3}F), {}^{4}T_{2}({}^{1}D) \rightarrow {}^{3}A_{2}({}^{3}F) \text{ and } {}^{4}T_{2}({}^{1}D) \rightarrow {}^{3}T_{2}({}^{3}F) \text{ transitions of the Ni}^{2+}$ ion, respectively. An emission at 506 nm is ascribed to d-d transitions ${}^{1}T_{2}({}^{1}D) \rightarrow {}^{3}A_{2}({}^{3}F)$ of the Ni²⁺ octahedral sites [41].



FIGURE 9.7 (a) Excitation and (**b & c**) emission spectra of Ni²⁺:Zn₂SiO₄ sol-gel derived powder

Optical analysis of Co²⁺:Zn₂SiO₄

The optical absorption spectrum of a $Co^{2+}:Zn_2SiO_4$ xero-gel is shown in **Figure 9.8**. The absorption peak in the range from 400 nm to 600 nm is assigned to the spin and electric-dipole allowed ${}^{4}A_{2g}({}^{4}F) \rightarrow {}^{4}T_{1g}({}^{4}P)$ transition. The broad absorption band in the NIR region, due to the tetrahedral complex of $[CoO_4]$, corresponds to ${}^{4}A_{2g}({}^{4}F) \rightarrow {}^{4}T_{1g}({}^{4}F)$ transition of the tetrahedrally co-ordinated Co^{2+} ion. The spectrum of the $Co^{2+}:Zn_2SiO_4$ xero-gel exhibits a broad band centred at 505-510 nm in the visible region and three small absorption bands in the NIR region. The energy-level diagram for Co(II) (3d⁷ configuration), in both octahedral and tetrahedral ligand field, presents three spin allowed transitions.



FIGURE 9.8

According to the literature, in the case of tetrahedral $[Co^{II}O_4]$ groups, two first spin-allowed bands fall in the infrared region (around 1400 nm and 1600 nm) and a third one is present in the visible region, usually manifesting as triple bands around 540 nm (green region), 590 nm (yellow-orange region) and 640 nm (red region). This triple band is attributed to the Jahn-Teller distortion of the T_d structure [38], due to an interaction between L and S. The high intensity of the tetrahedrally coordinated band is attributed to the mixing of 3d-orbitals with 4p-and ligand orbitals [36, 42].

By using standard Tanabe–Sugano diagrams of $T_d d^7$ system [40], the crystal field parameter, D_q of 405 cm⁻¹ and the Racah parameter *B* of 752 cm⁻¹ have been calculated for the 0.05 mol% Co²⁺:Zn₂SiO₄ xero-gel and presented in **Table 9.3**. By taking into account the relation of *C*=4.5*B*, Racah parameters were obtained with *C*=3388 cm⁻¹. Consequently, the ²E (²G) level is lower than ⁴T_{1g} (⁴P) level in Zn₂SiO₄, which is known as ²E. The crystal field splitting of the energy levels of Co²⁺ in the tetrahedral crystal field is similar to that of a d³ electronic configuration in an octahedral field, except for the value of crystal field parameter D_q , which is smaller in the tetrahedral case [42]. **Figure 9.9(a)** gives an excitation spectrum of Co²⁺:Zn₂SiO₄ nanopowders sintered at 1000 °C for 2 h, for an emission at 484nm. It presents two intense sharp excitation peaks at 384 nm and 442 nm, respectively. **Figures 9.9 (b)** and **(c)** show emission spectra of the 0.05 mol% Co²⁺:Zn₂SiO₄ sol-gel

Absorption spectrum of Co²⁺:Zn₂SiO₄ xero-gel

derived powder with two excitations at 384 nm and 442 nm. With λ_{exci} =384 nm, three emission peaks at 484 nm, 523 nm and 631 nm are seen, while with λ_{exci} =442nm again three emissions are observed, but this time at 484 nm, 540 nm and 602 nm. The emission of Co²⁺ ions at 631nm is assigned to the transition ²E (²G) \rightarrow ⁴A₂(⁴F) in T_d co-ordination [43]. The Meta stable ²E (²G) energy level is assigned to ⁴A₂ in the T_d co-ordinated Co²⁺ ion. The intense sharp emissions at 484 nm, 523 nm and 540 nm are attributed to electric dipole allowed transitions from the thermally populated ⁴T_{1g} (⁴P) [44].





Optical analysis of Mn²⁺:Zn₂SiO₄

Figure 9.10 shows the absorption spectrum of a $Mn^{2+}:Zn_2SiO_4$ xero-gel with absorption bands at 394 nm, 444 nm and 516 nm consistent with an octahedral symmetry for Mn^{2+} and Mn^{3+} ions. The absorption band at 444 nm, which is due to the $({}^{6}A_{1g}(S) \rightarrow {}^{4}T_{1g}(G))$ transition of Mn^{2+} , with a single spin allowed transition having a $3d^{5}$ -electronic configuration in the octahedral sites of the Zn_2SiO_4 xero-gel network [45-47]. With octahedral symmetry, the ground state of Mn^{2+} ion splits into lower ${}^{6}A_{1g}(S)$ and excited ${}^{4}T_{1g}(G)$ states elevated by 10Dq. By using the energy of this band, the crystal field factor ($D_q = 2252 \text{ cm}^{-1}$) of the $Mn^{2+}: Zn_2SiO_4$ xero-gel glass has been evaluated.



FIGURE 9.10 Absorption spectrum of Mn²⁺:Zn₂SiO₄ xero-gel



FIGURE 9.11

Excitation (a), and Emission spectra (b) of Mn^{2+} : Zn_2SiO_4 powder & insert figure (c) Green emission form Mn^{2+} : Zn_2SiO_4 under an UV lamp

Figure 9.11 presents both the excitation and emission spectra of $Mn^{2+}:Zn_2SiO_4$ with an emission band at 527 nm, which is assigned to the spin forbidden (${}^{4}T_{1g}(G) \rightarrow {}^{6}A_{1g}(S)$) transition with an excitation at 300 nm (${}^{6}A_{1g}(S) \rightarrow {}^{4}A_{1g}(G), {}^{4}E_{g}(G)$]) [48]. The spectral position of emission band explains about the site symmetry of Mn^{2+} ion. Following excitation by ultraviolet (UV) or visible light, the electrons in the ${}^{6}A1_{g}({}^{6}S)$ ground state of Mn^{2+} ions, are excited to the conduction band of Zn_2SiO_4 by photons, and the free electrons in the conduction band relax back to the ${}^{4}T_1$ (${}^{4}G$) excited state through a non-radiative process [30]. These excitation bands are followed by a radiative transition from the ${}^{4}T_1$ (${}^{4}G$) excited state to the ${}^{6}A1_{g}$ (${}^{6}S$) ground state, giving rise to a green light emission.

Optical analysis of Cr³⁺:Zn₂SiO₄

It is well known that the Cr^{3+} ion preferentially occupies an octahedral site in crystals and glasses. The colour, and absorption bands, changes with the ligand field strength [41]. **Figure 9.12** shows the absorption spectrum of a $Cr^{3+}Zn_2SiO_4$ xero-gel. The assignment of absorption bands will be discussed below based on the octahedral symmetry.



FIGURE 9.12 Absorption spectrum of the Cr³⁺:Zn₂SiO₄ xero-gel

The absorption bands are attributed to spin allowed electronic transitions of ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$ (578 nm) and ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$ (412 nm), respectively [49]. From the **Figure 9.12**, the band position (v₁= 1730 cm⁻¹) corresponds to the transition ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$, which enables the crystal field factor (namely Dq) to be evaluated. The wave number corresponding to the transition of ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$ is the band at 24271 cm⁻¹ (v₂). Using the following formula: B = $(2v_1^2 + v_2^2 - 3v_1v_2) / (15v_2 - 27v_1)$, the value of B is evaluated and found to be 698 cm⁻¹. The value of B is a measure of inter-electronic repulsion in the d-shell and is useful in discussing the ionic/covalent properties of Cr³⁺ ligand bonding. For the Cr³⁺ ion in octahedral symmetry, the spin forbidden transition ${}^{4}A_{2g}(F) \rightarrow {}^{2}T_{2g}(G)$ arise from within the same configurations of t_{2g}^3 . One weak absorption band is observed at 14663 cm⁻¹ (682 nm) and is assigned to the ${}^{4}A_{2g}(F) \rightarrow {}^{2}E_{g}(G)$ transition, with the help of

Tanabe-Sugano diagram [37]. The value of C is evaluated using the C/B=4.5 relationship and found to be 3141 cm^{-1} .



FIGURE 9.13

(a) Excitation and (b) emission spectrum of the Cr³⁺:Zn₂SiO₄ powder

Cr³⁺ ions have strong visible absorption bands due to the spin–allowed, but parity forbidden ${}^{4}A_{2g}$ → ${}^{4}T_{2g}$ and ${}^{4}A_{2g}$ → ${}^{4}T_{1g}$ transitions. The widths of these bands imply strong electronic coupling to vibrations of the local environment. Since the spin and parity forbidden ${}^{4}A_{2g}$ → ${}^{2}E_{g}$ and ${}^{4}A_{2g}$ → ${}^{2}T_{1g}$ absorptions are only weakly coupled to the vibrational spectrum [50], they appear as weak narrow lines superimposed on the ${}^{4}A_{2g}$ to ${}^{4}T_{2g}$ absorption band. Based on these assignments the values of band Dq, B and C are calculated and the following values D_q = 1691 cm⁻¹, B = 704.5 cm⁻¹ and C = 3170 cm⁻¹ give good agreement, both theoretically and experimentally, to the band positions [51]. **Figure 9.13** presents **(a)** the excitation and **(b)** the emission spectra of the Cr³⁺:Zn₂SiO₄ sample and shows the presence of an excitation band 557 nm (${}^{4}A_{2g}$ → ${}^{4}T_{2g}$ (F) and emission bands at 603 nm (${}^{2}T_{1g}$ (F) → ${}^{4}A_{2g}$ (F) and 624 nm (${}^{4}T_{2g}$ (F)) [52, 53].

Dielectric properties of TM^{3+/2+}:Zn₂SiO₄

It is well known that the conductivity and dielectric properties of ceramics are strongly dependent on the frequencies and temperatures employed in the investigations made. Hence, a systematic evaluation of these properties at different frequencies, various temperatures and by control over chemical composition is required to ascertain which kind of additives are needed to obtain good potential materials for a wide range of practical applications [53].

The dielectric constant is represented by $\varepsilon = \varepsilon' - i\varepsilon''$, where ε' is the real part of the dielectric constant and describes the stored energy, while ε'' is the imaginary part of the dielectric constant and describes the dissipated energy. **Figure 9.14** shows the combined plots for variation of the dielectric constant and dielectric loss properties for Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺ and Cr²⁺ doped Zn_{2-x}SiO₄ (x=0.05) sol-gel derived ceramic powders as a function of frequency (range 100 Hz to 1 MHz) at



FIGURE 9.14

Variation of dielectric constant and dielectric loss properties of (a) $Cu^{2+}:Zn_2SiO_4$, (b) $Ni^{2+}:Zn_2SiO_4$, (c) $Co^{2+}:Zn_2SiO_4$, (d) $Mn^{2+}:Zn_2SiO_4$ and (e) $Cr^{3+}:Zn_2SiO_4$ as function of frequency at room temperature

From **Figure 9.14**, it is clear that there is strong frequency dependence in the lower frequency region. The exponential decrease in the dielectric constant value with increasing frequency is a normal behaviour observed in the high frequency limit in most of ceramic materials. The dielectric constant decreases with the increase in frequency and becomes constant at high frequencies for all sample compositions. This type of dispersion behaviour can be explained on the basis of Maxwell–Wagner model type interfacial polarization [55, 56]. On the other hand, an increased dielectric constant value in the lower frequency region can possibly be related to a contribution from space charge/interfacial polarization. The increase in ε' with temperature is thought to be due to the bonding force between molecules/atoms with an increase in temperature. This permits the molecules/atoms to vibrate more and more, which in turn increases the polarization, hence produces an increase in the dielectric constant (ε').

According to this model, a dielectric medium is assumed to be made up of well conducting grains, which are separated by poorly conducting (or resistive) grain boundaries. Under the application of an external electric field, the charge carriers can easily migrate in the grains, but accumulate at the grain boundaries. This process can produce a large polarization and a high dielectric constant. The dielectric constant decreases with frequency as various polarisation processes cease at higher frequencies. The small conductivity of the grain boundary contributes to the high value of dielectric constant at low frequency [56]. The higher value of dielectric constant can also be explained on the basis of interfacial/space charge polarization due to the inhomogeneous dielectric structure. The polarization decreases with the increase in frequency and then reaches a constant value due to the fact that beyond a certain frequency of external field the hopping between different metal ions $(Zn^{2+}, TM^{3+/2+})$ cannot follow the alternating field [54].

In the case of cobalt doped samples, the observed increased dielectric constant for the biggergrained Co-substituted pellets may arise due to the change in the grain boundary thickness. In addition, during the sintering process, divalent cobalt can act as an acceptor dopant to substitute zinc, which is likely to occur in cobalt doped Zn_2SiO_4 grains. This would also impact on the dielectric properties. Apart from the grain boundary regional defects, the presence of interfacial polarization in these materials also plays an important role for the enhancement of the dielectric constant in the low-frequency region. Interfacial polarization arises due to the presence of micro heterogeneities in ceramics [56, 57] and can originate from low diffusion controlled thermochemical processes used for their preparation. Hence, as the dopant concentration increases, more zinc ions will be substituted by dopant ions, thereby decreasing the dielectric polarization, which in turn decreases dielectric constant.

Dielectric loss analysis

Loss tangent, or loss factor tan (δ), represents the energy dissipation in the dielectric system. **Figure 9.14** depicts a part of variation of the dielectric loss factor in the frequency range from 100Hz to 1MHz at room temperature. It was observed that tan (δ) decreases with the increase in frequency for all the compositions, which may relate to the space charge polarization. The decrease of tan δ with the increasing frequency is attributed to the fact that the hopping frequency of the charge carriers cannot follow the changes in the external electric field beyond a certain frequency limit. This type of variation in the dielectric losses is characteristic of the dipole orientation and electrical conduction and space charges. Thus, more dielectric relaxation can be observed, giving rise to more dielectric losses [58].

The higher dielectric loss that occurs at lower frequency is due to an accumulation of free charge at the interface between the electrolyte and the electrodes. At higher frequencies the periodic

reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The polar ionization due to the charge accumulation decreases, leading to a decrease in the value of the dielectric loss. In the case of the Ni²⁺ doped Zn₂SiO₄ sample, a relaxation effect in high frequency region is seen. As can be seen in **Figure 9.14d**, the frequency dispersion of the dielectric constant for Mn-doped Zn₂SiO₄ ceramics was strengthened, revealing additional relaxation. It may be inferred, that the increase of dielectric loss was linked to the polarization of defects resulting from Mn doping. Mn ions (Mn²⁺ and Mn³⁺) can be located either at zinc sites or at grain boundaries to form charged defects. For the origin of dielectric loss, it is reported that a low loss tangent has produced by addition of divalent and trivalent ions with ionic radii similar to that of zinc and demonstrated that the acceptors are compensated by oxygen vacancies. Decrease in dielectric loss is attributed to the formation of compensating defects originating from acceptor substitution [59].

Conductivity studies of doped Zn₂SiO₄ materials

The a.c conductivity starts to increase with increasing in frequency for all compositions of dopant, which is a common feature for the conductivity of ceramic materials. The total conductivity of the system is given by the following equation [57].

$\sigma = \sigma_0 (\mathbf{T}) + \sigma(\boldsymbol{\omega}, \mathbf{T})$ (4),

Where σ_0 is D.C. conductivity (σ_0) is independent of frequency. The second term σ pure A.C. conductivity due to the electron hoping between the metal ions. **Figure 9.15**, shows the variation of a.c conductivity with frequency range 100 Hz to 1 MHz, at room temperature, for TM3+/2+:Zn2SiO4 (TM= Cr3+, Mn2+, Co2+, Ni2+ & Cu2+). It has been observed that the A.C. conductivity gradually increases with an increase in frequency of the applied A.C. field. This is because the increase in frequency enhances the electron hopping of charge carriers among localized states [60]. It was reported, that A.C. conductivity increases with an increase in dopant concentration up to 0.5 mol% and then decreases at 0.75 mol% (and above) for Ni²⁺:Zn₂SiO₄ [61]. This may be attributed to the fact that the dopant of TM³⁺/²⁺ ions are acceptor dopants for Zn₂SiO₄. However, the substitution of Zn²⁺ with Ni²⁺ can only take place up to a certain limit [62]. Thus, the increase in the dopant conductivity. However, as the substitution of Zn²⁺ with Ni²⁺ is limited there is a decrease for 0.50 mol%. It may be that the dopant in the TM^{3+/2+}: Zn₂SiO₄ systems are acceptors for Zn₂SiO₄ and, are usually, compensated by the formation of oxygen vacancies.

Thus, the increase in the dopant concentration increases the number of oxygen vacancies, which results in an increase in the free electron density and conductivity. However, when the introduction of Ni^{2+} exceeds a certain limit, the superfluous Ni^{2+} that cannot substitute Zn^{2+} further, will segregate to the grain boundary interfaces. The segregation of Ni^{2+} then blocks the building and transportation of electrons and other defects, thereby decreasing the conductivity [63].

At low frequencies, where the conductivity is constant, the transport takes place on infinite paths. For a region of frequencies where the conductivity increases strongly with frequency, the transport is dominated by contributions from hopping infinite clusters. Finally, a region where the high frequency cut off starts to play a role is encountered. The electrical conduction mechanism has been explained in terms of the electron hopping model [61-64]. As the frequency of the applied electric field increases, the hopping frequency of the applied electric field increases. Also the hopping frequency of electrons between cation states ($Co^{3+}\leftrightarrow Co^{2+}$ and $Ni^{3+}\leftrightarrow Ni^{2+}$) at adjacent

octahedral site increases due to thermally active electrons. This then leads to increase in the conductivity. Consequently, the increase in frequency enhances the hopping frequency of charge carriers resulting in an increase in the conduction process, thereby increasing the conductivity.



FIGURE 9.15

Variation of ac conductivities of (a) $Cu^{2+}:Zn_2SiO_4$, (b) $Ni^{2+}:Zn_2SiO_4$, (c) $Co^{2+}:Zn_2SiO_4$, (d) $Mn^{2+}:Zn_2SiO_4$ and (e) $Cr^{3+}:Zn_2SiO_4$ as function of frequency at room temperature

Conclusions

Doped Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺ and Cr³⁺:Zn₂SiO₄ powders have been successfully synthesised by a solgel route. Well defined sharp peaks have been obtained from the powder X-ray diffraction patterns and their EDAX profile confirming the presence of dopant ions in the host matrix. Compositional analysis (EDS) ascertained the existence of Zn, Si, O, Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺ and Cr³⁺ in the synthesized materials. Both crystal field (D_q) and energy level characteristic Racah (B,C) parameters have been computed based on measured absorption spectra profiles and photoluminescence of the Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺& Cr³⁺: Zn₂SiO₄ samples. The dielectric constant (ϵ ') and loss tangent (tan δ) decrease with increasing the frequency of applied electric field. It was concluded that the tunability was linked to both the dielectric constant and the grain size. This can be explained by the space charge polarization process based on the Maxwell–Wagner two layer models. The obtained dielectric constant and dielectric loss tangent results of the studied samples at higher frequencies indicate that these materials have significant potential for microwave-integrated circuits.

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