Investigating the Influence of Titanium ion Substituted Cd-Al-Mn Ferrite Composites on the Structural, DC Resistivity and Electrical Switching

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Abstract

A nano-crystalline spinel ferrite (NC-SF) composites were synthesized using the standard ceramic method and were analyzed by several analytical techniques. The XRD characterization validates the production of a cubic spinel arrangement. Furthermore, XRD analysis showed that the bond length and ionic radii enlarge on A-sites and reduce slightly on B-sites with the increase in the content of Mn-Ti. Moreover, XRD analysis revealed that the crystallite size of Cd-Ti-Al-Mn lies in the range of 22.83-24.44nm. Additionally, the porosity of the Cd-Ti-Al-Mn ferrite samples reduces with increasing the content of Mn-Ti. The FT-IR spectra show one high-frequency band and three low-frequency bands in the range of 400-600 cm⁻¹. The grain size was observed by SEM images to be uniformly distributed and lies within the range of ~0.66-1.18µm. The DC resistivity of the ferrite composite became greater with increasing the content of Mn-Ti. Moreover, the composite behaves electrically as semiconductor. The investigated Cd-Ti-Al-Mn ferrite composites exhibited current controlled negative resistance (CCNR) type of electrical switching characteristics at room temperature. The value of the switching electric field was noted to enlarge with the increase in the content of Mn-Ti. Additionally, there was no ageing observed for electrical switching property in the investigated ferrite composites

Keywords: DC Resistivity, Curie temperature, CCNR type electrical switching, Hopping length.

Introduction

Spinel has a crystal structure of a face-centered cubic (FCC). Thus, spinel ferrite structure has eight tetrahedral and sixteen octahedral sites that are partially fully occupied with cations. Tetrahedral and octahedral sites are surrounded by four and six oxygen anions [1]. Spinel-type of ferrites has a general chemical formula, $M^{2+}Fe_2^{3+}O_4^{2-}$, where M2+ presents a divalent metal cation and Fe_2^{3+} presents a trivalent iron cation and O_4^{2-} presents an oxygen anion [2]. Spinel-type of ferrites is emerging material since it possesses superior chemical stability, mechanical hardness and magnetic and electric properties. Spinel ferrite materials have been used in numerous applications such as nonvolatile memory (NVM) devices [3-5], water and wastewater treatment [6], drug delivery [7-10], power electronics [11], sensors [12-13], microwave devices [14-15] and electrical switching [16]. The structural, morphological, electrical, optical, magnetic, dielectric and electrical switching properties of spinel ferrite materials were extensively studied [17-20]. Manganese is a rarely available metal and also costly [21], whereas titanium is the ninth most abundant metal in the earth's crust [22]. Titanium can be incorporated in ferrites to reduce ferrous contents [23]. Cadmium (Cd) and zinc (Zn) are two nonmagnetic divalent cations and when they are substituted in ferrites, they occupy tetrahedral A-site [24]. The cadmium-containing ferrite has a normal spinel arrangement with Cd2+ and Fe3+ cations on tetrahedral (A) and octahedral (B) sites, respectively [25]. The influence of aluminum-substitution on the electrical properties of manganese-nickel-zinc (Mn-Ni-Zn) ferrite composites was studied by Sattar et al. [26]. Rao et al. reported a raise in the DC resistivity and Curie temperature with substituting Ti4+ in Ni-Zn ferrite composites [27]. Zuo et al. studied manganese ferrite (MnFe2O4) composite and they reported that the composite was observed to be a combination of inverse and normal spinel ferrites and at high temperature (>9000C), the Mn2+ cations transferred from site A to site B [28].



The current controlled negative resistance (CCNR) is an electrical switching behavior that was first discovered and reported by Yamashiro while he was studying CuFe2O4 ferrite composite [29]. Kamble et al. studied polycrystalline Cu-CdFe2O4 ferrite composite and they reported that the lattice constant for the ferrite was found to be enlarged with increasing the quenching temperature [30]. They also noted that quenching has no effect on the electrical switching properties of the composite. Vasambekar et al. reported that the CCNR type of electrical switching was observed in paramagnetic materials [31]. They also observed that cadmium ferrite displaied the lowest value of switching electric field, no ageing effect and reproducible switching phenomenon. Saija et al. reported that applying high electrical field induced CCNR type of electrical switching in Ti+4 substituted manganese-zinc ferrite composite [32]. They demonstrated that the strength of the electric field and the thermal energy that are essential for inducing electrical switching enlarge with increasing the concentration of manganese-titanium. The electrical switching property of Cr3+ and Al3+ substituted NiFe2O4 [33, 34] and Cd-Co ferrite thin films was reported [35]. They found that the electric field that derives the resistive switching enlarges and reduces with the increase in the contents of chromium and aluminum, respectively.

Previously we reported on the effect of sintering temperature and grain size on electric switching property in cadmium ferrites [16-17]. Here we report on the structural, DC electrical resistivity and electrical switching properties of Ti4+substituted Cd-Al-Mn ferrites at room temperature. That is Mn was replaced with Ti in Cd-Al-Mn ferrites and then the changes in the properties of these ferrites were observed.

Materials and Methods

Materials

The nanocrystalline spinel ferrites (NC-SF) with chemical formula $Cd_{0.3}Mn_{0.7+x}Ti_xAl_{0.1}Fe_{1.9-2x}O_4$ (x= 0, 0.05, 0.10, 0.15 and 0.20) were fabricated by traditional ceramic method. The starting materials were AR grade. Cadmium Oxide (Himedia, Mumbai, India), Titanium Dioxide (Thomas Baker, Mumbai, India), Aluminum Oxide (Thomas Baker, Mumbai, India), Manganese (II) carbonate (Himedia, Mumbai, India) and Ferric Oxide (Thomas Baker, Mumbai, India). Potassium Bromide (ACS reagent, 99.0%, KBr), Acetone (\geq 99.9%), Polyvinyl Alcohol (99.8% hydrolyzed, PVA) and Silver Paste were purchased from Sigma-Aldrich (Mumbai, India) and were used as received.

Sample Preparation

The purchased materials were scaled according to the needed stoichiometry percentage. They were then mixed and milled in an agate mortar along with solvent, acetone. These powders were pre-sintered in a muffle furnace for 12 hours at 1000°C. After the furnace was cooled down, the powders were further milled in an agate mortar with the assistance of acetone and then sintered in a muffle furnace at a temperature of 1100°C for 24 hours. Moreover, the powders were mixed with solvent, acetone and 5% of binder, polyvinyl alcohol, milled in an agate mortar, mixed with 10mm KBr, and pressed at 5 Ton/cm2 for 5 min on a Carver 3851 Press (Thomas Scientific, Swedesboro, NJ USA) to form 1 cm in diameter and 0.5 cm in thickness pellets. The formed KBr pellets were finally sintered at a temperature of 1100°C for 2 hours.

Characterization

The ferrite composites in powder form were characterized by X-ray diffraction technique. The X-ray diffraction patterns were recorded at step size and time of 0.020 and 1 second, respectively. The XRD measurements were done in angular range 100–1000 (20) at 40 kV, 25 mA with Cr-K α radiation (λ = 2.29165 A°) on Philips PW-3710 X-ray powder diffractometer (Philips, Amsterdam, Netherlands). FT-IR spectra were recorded at room temperature by averaging 64 scans recorded at a rate of 1 scan per second in a wavelength range of 350-800cm-1 on Perkin-Elmer Spectrum one spectrophotometer (Perkin-Elmer, CA USA) using pressed KBr pellet. SEM images of the investigated ferrite were used to evaluate the microstructure of fractured surfaces of the pellets using (Hitachi High-Technologies Corporation, Tokyo, Japan) at an acceleration voltage of 10 kV. In order to obtain a good electrical conductivity, gold was sputtered onto the ferrite samples prior to SEM imaging.



Electrical and thermal measurements

The pressed and sintered Cd-Al-Ti-Mn ferrite composite pellets were gently polished before the DC resistivity measurements to ensure a smooth and oxide free surface. Furthermore, a thin film of silver paste was applied on the pellets surface to obtain a conductive layer for a good ohmic contact during electrical measurements. The DC resistivity measurements were acquired by a two-probe method using Keithley Electrometer (Tektronix, Oregon USA) in a temperature range from room temperature to 750°K.

The Curie temperature of ferrite material is defined as the temperature at which an ordered ferrimagnetic material becomes a disordered paramagnetic [36]. Curie temperature, Tc, is extracted from the logarithm of the DC resistivity (p) vs. the inverse of the temperature (T) of the samples plot. The slope of the resistivity will suddenly change at the Curie temperature corresponding to the change in the activation energy (EA) due to the magnetic transformation from ferrimagnetic to paramagnetic [37]. Moreover, Curie temperature was determined using the modified Lorria-Sinha method [38]. To summarize this method, an electromagnet was powered by 15 volt. The pressed and sintered Cd-Al-Ti-Mn ferrite composite pellets were attached to the electromagnet and then were placed at the center of a furnace equipped with a temperature controller. The temperature of the furnace was gradually enlarged to the Curie temperature at which pellets change from ferrimagnetic to paramagnetic and the pellets were suddenly detached from the electromagnet.

In order to study the electrical switching property of the ferrite composites, the I-E characteristics of the samples under investigation was measured by the two probe method in a voltage range of 0-600V at room temperature using Aplab high voltage DC power supply (H1010, Maharashtra, India) and Meco 81K multimeter (8000, Maharashtra, India).

Results and Discussion

Structural properties

The X-ray diffraction patterns indicating (h k l) values of each peak corresponding to the samples x = 0, 0.05, 0.10, 0.15 and 0.20 of Cd_{0.3}Mn_{0.7+x}Ti_xAl_{0.1}Fe_{1.9-2x}O₄ (Cd-Mn-Ti-Al-Fe₂O₄) ferrite structure is presented in **Fig**.1. The existence of (220), (311), (222), (400), (442), (333) and (440) peaks in the XRD-patterns validates the configuration of cubic spinel system. Furthermore, the high reactivity at high temperature between Mn²⁺ and Fe³⁺ results in the creation of perovskite phase that is presented by an extra perovskite peak located between (220) and 311 planes [39, 40]. Zhong *et al.* reported that MnCO₃ decomposed in air at temperature beyond 500°C. Furthermore, they reported that Mn ions changed their valence in air, and Mn²⁺ and Mn³⁺ cations have a strong site preference for A-site and B-site, respectively [41]. The samples in the present investigations were sintered at 1100°C and the phase of Mn₂O₃ was observed in the XRD interference pattern.

The lattice constant a) of the investigated ferrite samples (Cd-Al-Ti-Mn) is calculated by using the following equation [42], as following:

$$a = \frac{1}{d_{hkl}} \sqrt{h^2 + k^2 + l^2}$$
(1)

where d_{hkl} - is the interplaner distance and h, k and l are miller indices.

The interplanar distance, d_{hkl} can be determined using Bragg's law:

$$n\lambda = 2d_{hkl}\sin\theta \tag{2}$$

where λ is the diffraction wavelength, θ is Bragg's diffraction angle and n is





Figure 1. XRD diffractogram of $Cd_{0.3}Mn_{0.7+x}TixAI_{0.1}Fe_{1.9-2x}O_4$ (x = 0.00, 0.05, 0.10, 0.15 and 0.20).

The change of the values of lattice constant with respect to the change in the content of Mn-Ti is graphed and presented in **Fig.**2. It can be seen from **Fig.** 2 that the lattice constant enlarges with the increase of the content of Mn-Ti. This may be caused by the discharge of lattice strain when the spinel composite reaches the inverse spinel ferrite state. Since the smaller ionic radii of Fe^{3+} (0.064 nm) are being replaced by the larger ionic radii of Ti^{4+} (0.068 nm), the increase in lattice constant value implies that the position of Mn^{2+} and Ti^{4+} cations in the host matrix were exchanged. Comparable results were reported by Dogra *et al.* [43] and Saija *et al.* [32] while they were studying Mn-Ti substituted Ni-Mg and Zn-Al ferrite, respectively.





Figure 2. The changes of the lattice constant value with respect to the change of the content of Mn-Ti.

The average crystallite size (D) of Cd-Al-Ti-Mn ferrites was calculated from the most intense peak (311) of the XRD diffractogram by using Debye Scherer equation [44]:

$$D = \frac{0.94 \lambda}{\beta \cos \theta}$$
(3)

where, λ is the wavelength of the X-ray, β is the full width half maximum (FWHM) and θ is the Bragg's diffraction angle. The parameter β can be obtained using the following equation [45]:

$$\beta = \left(\beta_F^2 - \beta_S^2\right)^{1/2} \tag{4}$$

where β_F is the full width half maximum of (311) peak and β_S is the standard instrumental broadening.

The average crystallite size of Cd-Al-Ti-Mn ferrites lies in the range of 22.83 to 24.44nm and was observed to vary randomly. The values of the crystallite size for different contents of Mn-Ti are presented in **Table1**. These results show strong agreement with the results reported by lyer *et al.*, *where* $Mn_{1-x}Cd_xFe_2O_4$ ferrite structure was fabricated and studied [25].

Density contributes significantly in varying the properties of polycrystalline ferrites to fit specific applications. The X-ray density (p_{x} , kg/m³) of Cd-Al-Ti-Mn ferrites is calculated by using the following equation [46]:

$$d_x = \frac{\mathcal{B}M}{Na^3}$$

where `8' is the number of molecules in a unit cell of spinel lattice, M is the molecular weight of the sample, N is the Avogadro's number and `a' is the lattice parameter.

(5)

The values of the X-ray density for different contents of Mn-Ti are presented in **Table**1. As X-ray density is inversely proportional to the lattice constant according to Eq. (5), the value of X-ray density was reduced



with the increase in the content of Mn-Ti as can be noted from **Table** 1. This is attributed due to the ionic concentration difference between Mn-Ti and Fe. Furthermore, the reduction in X-ray density is caused by the decrease in mass that overtook the reduction in the volume of the unit cell. Comparable results were revealed by Patange *et al.*, when they synthesized and investigated NiAlFe₂O₄ ferrite compositions [34].

Conte nt of	Lattice consta nt (A°)	Crystallit e size D (nm)	X-ray densit y d _x (g/c m ³)	Physic al densit y d_x (g/cm ³)	Porosit y P (%)	Bond Length (A [.])		Ionic radii (A [.])		Hoping length	
Mn-Ti						A-0	B-O	r _A	r _B	L _A	L _B
0.00	8.6213	24.44	5.0930	4.985	2.12	2.09 1	2.02 6	0.74 1	0.67 6	3.73 3	3.04 8
0.05	8.6235	22.99	5.0761	4.972	2.05	2.10 3	2.01 5	0.75 3	0.66 5	3.73 4	3.04 9
0.10	8.6312	22.83	5.0422	4.943	1.97	2.12 2	2.01 1	0.77 2	0.66 1	3.73 7	3.05 1
0.15	8.6487	24.17	5.002	4.912	1.81	2.13 4	2.01 0	0.78 4	0.66 0	3.74 4	3.05 7
0.20	8.6513	23.65	4.989	4.882	1.78	2.14 2	2.00 7	0.79 2	0.65 7	3.74 6	3.05 8

Table 1. Structural data of Cd_{0.3}Mn_{0.7+x}Ti_xAl_{0.1}Fe_{1.9-2x}O₄ (x= 0.0, 0.05, 0.10, 0.15 and 0.20) system

The physical density (d_P , kg/m³) of Cd-Al-Ti-Mn ferrites are calculated by using the Archimedes principle using the following equation.

$$d_P = \frac{W.d}{W - W'} \tag{6}$$

where W is the weight of the ferrite sample in air, W' is the weight of the sample in xylene and d is the density of xylene.

The values of the physical density for different contents of Mn-Ti are presented in **Table**1. It can be seen that the physical density of Cd-Al-Ti-Mn ferrite compositions was reduced with the increase of the content of Mn-Ti. The reduction of the physical density may be caused by the decrease of the atomic weight as a result of substituting Mn-Ti ions for the higher-density Fe^{3+} ions. The atomic weights of Fe^{3+} and Mn-Ti are 55.847 Da and 54.93-47.88 Da, respectively. The X-ray density (d_X) values are slightly larger than the physical density (d_X) which agrees with the results reported by Gadkari *et al.* in case of Mg-Cd ferrites [47]. This is due to the fact that the mass to volume ratio of Fe^{3+} is larger than the mass to volume ratio of the content of Mn-Ti. Moreover, this may be due to the creation of pores during the sample formation or the sintering process. The variation of X-ray and physical densities is presented in **Fig.**3, which shows a decreasing trend with Mn-Ti content.





Figure 3. The variations of the X-ray and physical densities with respect to the content of Mn-Ti.

Porosity is defined as the ratio of the difference between the theoretical (X-ray) density and the physical density to the theoretical density. Thus, the porosity percentage (P %) of Cd-Al-Ti-Mn ferrites is calculated by using the following equation [48]:

$$P = 100 \left(1 - \frac{d_p}{d_x}\right)\% \tag{7}$$

The values of the porosity of Cd-Al-Ti-Mn ferrites under investigation are presented in **Table** 1. It can be seen that the porosity of the samples was reduced with the increase of the content of Mn-Ti. This is due to the fact that the melting point of Mn-O is lower than that of the Fe-O [49, 50]. The variation in the porosity is due to the microstructural changes taken place during the sintering process of the ferrite synthesis. The number of pores is increasing at a higher sintering temperature. This leads to the enlargeent of the effective area of the grain causing single grains to get physically closer. This leads to a greater densification or higher porosity of the ferrites [25].

The X-ray diffraction data is used to calculate the bond lengths (A-O and B-O) of spinal structure by utilizing the equations reported by Standley [42]:

$$A - O = \left(u - \frac{7}{4}\right)a\sqrt{3}$$

$$B - O = \left(\frac{5}{8} - u\right)a$$
(8)
(9)

where u is the oxygen ion parameter.

The tetrahedral and octahedral ionic radii (r_A and r_B) of the investigated spinal structure are given by Stanley's equation:

$$r_{A} = \left(u - \frac{1}{4}\right)a\sqrt{3} - r(O^{-2})$$

$$r_{B} = \left(\frac{5}{8} - u\right)a - r(O^{-2})$$
(10)
(11)

where $r(O^{-2})$ is the ionic radius of oxygen.

The obtained values of the ionic radii and bond length on A-site and B-sites are summarized in **Table1**. The bond length and ionic radii were found to enlarge and reduce slightly on A-sites and B-sites, respectively, with the content of Mn-Ti. Comparable results were reported by Kadam *et al.* [40] in Sm⁺³ substituted Co-Zn ferrites. This is caused by the Ti⁴⁺ cations prefer octahedral site (B-site), and replace Fe³⁺ cations in the



spinel structure. The smaller ionic radius of Fe^{3+} (0.064 nm) is being replaced by the larger ionic radii of Ti^{4+} (0.068 nm) [43].

The space between magnetic ions and jumping length of tetrahedral (A-site), L_A, and octahedral (B-site), L_B, are determined by following relations:

$$L_A = a \frac{\sqrt{3}}{4}$$
 and $L_B = a \frac{\sqrt{2}}{4}$ (12)

The calculated values of the hopping length of A-site and B-site are shown in **Table1**. It can be seen that the hoping lengths similar to the lattice contestant enlarged with increasing the content of Mn-Ti. The increase in hoping lengths is due to the replacement of Fe^{3+} ions of smaller ionic radius with Ti^{4+} ions of larger ionic radius. Shirsath *et al.* similarly showed that hopping lengths L_A and L_B enlarged with the increase of the content of Mn in Ni-Zn ferrite [51].

The FT-IR spectra of Cd-Mn-Ti-Al ferrite of all the synthesized samples are presented in Fig. 4. By looking at Fig. 4, one can see four bands in the ferrite structure in the range of 350–800 cm⁻¹. The FT-IR spectra for several ferrite composites were reported by Waldron [52]. Literature revealed that ferrite structures with inverse and normal cubic spinels have four IR bands presenting the four fundamental frequencies [53]. The values of absorption bands υ_1 , υ_2 , υ_3 and υ_4 are presented in **Table** 2. It can be noticed from **Table** 2 that two major absorption bands are near about 400 cm⁻¹ and 600 cm⁻¹ of octahedral and tetrahedral sites, respectively. Gadkari et al. observed two major absorption bands in Mg-Cd ferrite within the range of 350-800 cm⁻¹ [47]. The high-frequency band, v_1 , is in the range of 580-590 cm⁻¹ and is related to the intrinsic vibrations of the tetrahedral group. The low-frequency bands, v_2 and v_3 , lie in the ranges of 460-470 cm⁻¹ and 390-395 cm⁻¹, respectively, because of the octahedral metal complexes. The fourth observed bands, v₄, at the range of 360-370 cm⁻¹ can be assigned to the divalent tetrahedral vibrations. Hemeda et al. [54] reported that the shift in the v_1 and v_2 bands was dependent on the compositions of the ferrite composites. The IR absorption band v_2 at the octahedral B-sites was shifted to lower frequency, which is caused by the replacement of Fe³⁺ ions by Mn⁴⁺ ions. This value represents the contribution of the ionic bond Fe-O in the lattice. The band υ_1 shifted slightly towards the lower frequency side with the increase of the content of Mn-Ti. This observed shifting was due to the enlargement of sites radius that cause the reduction of the primary frequency, and therefore the middle frequency shifted towards the low frequency side and the opposite effect happened for v_2 .





Figure 4. Infrared absorption spectra of $Cd_{0.3}Mn_{0.7+x}Ti_xAl_{0.1}Fe_{1.9-2x}O_4$ (x = 0, 0.05, 0.10, 0.15 and 0.20). Table 2. Structural, electrical and switching data for $Cd_{0.3}Mn_{0.7+x}Ti_xAl_{0.1}Fe_{1.9-2x}O_4$ (x=0.0, 0.05, 0.10, 0.15 and 0.20) structure

Mn-Ti Content	FT-IR Absorption bands (cm ⁻¹)				Room temperature resistivity	Activation energy (eV)		Curie temperature (^o K)		Electrical field E (V/cm)	
	U 1	U2	U3	U 4	ο logρ (Ω cm)	Para- region (E _p)	Ferri- rigion (E _f)	Loria Sinha	DC Resisti- vity	-	
0.00	587.58	466.81	395	370	12.15	0.966	0.552	480	488	1600	
0.05	587.47	465.59	394	370	12.50	0.981	0.579	490	493	1750	
0.10	586.75	464.89	393	364	12.83	1.002	0.602	495	498	1850	
0.15	585.84	464.53	392	362	12.94	1.010	0.606	505	503	1900	
0.20	585.80	464.34	390	360	13.12	1.021	0.640	507	508	2150	

The microstructure of the ferrite samples affects physical and mechanical properties. Microstructure studies for the ferrite materials are necessary to understand the link between their properties and behavior in numerous applications. The SEM images for the microstructure of a fractured surface of Cd-Mn-Ti-Al ferrites pellet are depicted in **Fig**.5. It can be noted from the figure that some grains are found to be agglomerated and some grains are homogeneously dispersed to the whole surface of the pellet. Furthermore, it can be noted from **Fig**. 5 that the grain size of the materials reduces with increasing the content of Mn-Ti. This is due to the smaller ionic radius of Fe³⁺ is being substituted by the larger ionic radii of Ti⁴⁺. The average grain size of the particle of Cd-Mn-Ti-Al ferrites was found to be about ~0.66-1.18µm.





Figure 5. SEM micrographs of $Cd_{0.3}Mn_{0.7+x}Ti_xAI_{0.1}Fe_{1.9-2x}O_4$ (x = 0, 0.20).

DC electrical resistivity

The variation of the logarithm of the DC electrical resistivity, Log (ρ), with the inverse of the temperature of the samples is presented in **Fig**.6. By looking at the figure, it can be noted that the electrical resistivity of Cd-Mn-Ti-Al ferrites reduces with increasing the temperature values exhibiting semi-conducting behavior. The resistivity dependence of temperature is calculated by Arrhenius relation as presented in Eq. 11 [55].

$$\rho = \rho_o e^{\left[\frac{E_A}{KT}\right]}$$

(13)

where ρ_o is the pre-exponential factor (Ω .cm), K is Boltzmann constant (eV K⁻¹), E_A is the difference between the activation energies in ferromagnetic (Ef) and paramagnetic (Ep) regions (eV) and T is the absolute temperature ($^{\circ}$ K).



Figure 6. The variation in the values of logarithm of the DC electrical resistivity, Log (ρ), against the inverse of temperature of the samples, 10³/T, for Cd_{0.3}Mn_{0.7+x}Ti_xAl_{0.1}Fe_{1.9-2x}O₄ (x = 0, 0.05, 0.10, 0.15 and 0.20).



The change in the DC electrical resistivity log (ρ) and the porosity (%) at room temperature as a function of the content of Mn-Ti in Cd-Al-Mn ferrite is presented in **Fig**. 7. It can be noted that the DC electrical resistivity was found to be enlarged from 12.1×10^6 to $13.2 \times 10^6 \Omega$ cm with the enlargement of the content of Mn-Ti. The addition of Mn²⁺ reduces the concentration of Fe²⁺ ions on B-sites. This is caused by the fact that the incorporation of Mn ions in B-site and Ti ions in A-site and B-site of the ferrite may reduce the concentration of Fe²⁺/Fe³⁺ ion pairs. Comparable results were reported by Saija *et al.* [32] in case of Ti⁴⁺ replaced by Mn-Zn ferrites. Furthermore, it can be seen from Fig. 7 that the DC electrical resistivity reduces while the value of porosity enlarges with the increase of the content of Mn-Ti. Literature revealed that as the porosity of ferrite samples raise, the number of pores, scattering centers and vacancies, for the electric charge carriers enlarges, leading to an enlarge in the DC resistivity. This is attributed due to changes in the pore size, grain size and scattering [56].



Figure 7. Room temperature resistivity, Log (p), and porosity, (%), as a function of the content of Mn-Ti.

The electrical conductivity in Cd-Mn-Ti-Al ferrites is due to the exchange of electrons from Fe²⁺ to Fe³⁺. The activation energy is required for this electron exchange. The hopping or jumping of electrons affected by the space between the ions and requires sufficient energy that is known as the activation energy, E_A [57]. The jumping of electrons between Fe²⁺ and Fe³⁺, Ti³⁺ and Ti⁴⁺ and Mn²⁺ and Mn³⁺ causes the electrical conductivity within the ferrite. The additions of Mn-Ti ions in the ferrite reduce the concentration of Fe²⁺ ions. The subsequent equilibrium exists in the sintering process and causes this reaction: Fe²⁺ + Mn³⁺ \rightarrow Fe³⁺ + Mn²⁺. Due to the enlargement of the content of Mn, Mn³⁺ ions are oxidized and become Mn²⁺. Furthermore, this decree and enlarges the possibility of electron jumping and the value of DC resistivity, respectively. The enlarged number of octahedral Ti⁴⁺ ions act as scattering centers for the Fe²⁺ - Fe³⁺ conduction similar to Mn²⁺ ions.

By looking at **Fig**. 6, one can see that slope of the lines that represent the changes of the logarithm of the DC resistivity with respect to the inverse of the temperature of the samples has a value in the low temperature region and a different value in the high temperature region. The slope in the low temperature region corresponds to ferrimagnetic materials and it changes to paramagnetic in high temperature region. This phase transition from ferromagnetic to paramagnetic is caused by the energy difference at both states. This state transition occurs with respect to the change in temperature, which indicates temperature dependence of the energy of each phase. The activation energies in the ferrimagnetic region (E_f) and paramagnetic region (E_p) are calculated from the slop of each line in **Fig**. 6 using the following equation [58]:



$$E = slope \times 4.606 \times 8.62 \times 10^{-5} eV$$

(14)

The values of E_f and E_p are shown in **Table** 2. It can be seen that the values of E_p , is higher than that of E_f . This validate the transition from the ordered ferromagnetic state in which electronic current dominates the conductivity within the ferrite material to the arbitrary paramagnetic phase in which ionic current with higher activation energy dominates the conductivity within the material. Furthermore, it was found that the activation energies rise with the increase of the content of Mn-Ti. This rise is caused by the creation of larger number of oxygen vacancies, which is in agreement with the results reported by Ajmal *et al.* in Ni-Zn ferrites [59].

The change of the Curie temperature values with different content of Mn-Ti (x) is presented in **Fig**. 8. Curie temperature is measured using the DC resistivity graph and Lorria-Sinha method. Curie temperature values obtained from both methods show a strong agreement, as can be seen from **Table** 2. Moreover, one can notice that the values of Curie temperature enlarge with the enlargement of the content of Mn-Ti. The change in Curie temperature value with respect to the change in the content of Mn-Ti is due to the change in A-B exchange interaction strength which in turn depends on the cation distribution (between A and B sites). In addition, the thermal energy required for the alignment of the magnetic moment rises, leading to the increase in the value of Curie temperature [27].



Figure 8. The variation in Curie temperature values with different content of Mn-Ti.

Switching properties

The I-E characteristics of the Cd-Mn-Ti-Al ferrites at room temperature are presented in **Fig.** 9. It can be seen from the figure that the DC electric current is initially increasing steadily with a rapid enlarge in the electric field. Once it reached a threshold value (switching value, 1500-1750 v/cm), it quickly enlarges with the reduction of the electric field. This shows that the current flew through a non-stabile conduction state and went into a very high conduction state. That is the conductivity was switched between two regions [31, 34-35]. Thus, the current controlled negative resistance (CCNR) type of electrical switching (also known as resistive switching) is observed in all prepared Cd-Mn-Ti-Al ferrites [16-17, 31-32, 33-34], as can be seen from **Fig.** 9. The variation in the value of the switching electric field with respect to the content of Mn-Ti is presented in **Table**. 2. It can be noticed that the electric field enlarges with the increase of the content of Mn-Ti. This is because of the subsequent enlargement of the lattice dimension and the reduction in Fe³⁺ ion concentrations from the octahedral B-site [32]. In Ti⁴⁺ substituted Cd-Al-Mn ferrites, the switching



phenomenon was mainly explained on the basis of the sintering temperature [16], grain size [17], structure [29, 30], lattice constant, cation distribution [31], Joule self-heating [31] and space charge limited current (SCLC) [60]. Previously, we reported that the grain size was reduced with the decrease in the switching electric field for 5% rare earth ions ($R = Sm^{3+}$, Y^{3+} and La^{3+}) added cadmium ferrite [17] and also the effect of sintering temperature on switching properties of cadmium ferrite [16]. Yu *et al.* reported that the resistive transparent switching layer of Al doped ZnO is used for random access memory devices [61]. The switching properties of the all prepared Cd-Mn-Ti-Al ferrites samples were reinvestigated after two weeks, the cycle was repeated and it was successfully reproducible. Therefore, it was confirmed that there was no ageing effect observed in the prepared ferrite composites. The conduction mechanism is also used to classify the resistive switching. Resistive switching could be originated from the configuration and rupture of conductive filaments in a non-conductive matrix as shown in Fig. 10. This might be related to both unipolar and bipolar resistive switching behaviors, as it was well explained by Akihito Sawa [62].



Figure 9. I-E characteristics (resistive switching) of $Cd_{0.3}Mn_{0.7+x}Ti_xAI_{0.1}Fe_{1.9-2x}O_4$ (x = 0, 0.05, 0.10, 0.15 and 0.20).





Figure 10. Photograph of rupture formation of the investigated ferrite pellet.

Conclusions

The XRD validated the biphasic nature of the ferrite samples. The lattice constant was found to be increasing with the enlargement of the content of Mn-Ti. The crystallite size of the samples lies in the range of 22.83-24.44nm. Bond length (A-O) and ionic radii (r_A) on A-sites enlarge, whereas bond length (B-O) and ionic radii (r_B) on B-site reduces with the content of Mn-Ti. The porosity of the samples was reduced with the increase in the content of Mn-Ti. The FT-IR study showed one high-frequency band and three low-frequency bands. The grain size lies in the range of ~0.66-1.18 µm. The DC resistivity of Cd-Al-Mn ferrites was reduced with the raise of the temperature due to its semi-conducting behavior. The value of the activation energy in the paramagnetic region is higher than that of the ferromagnetic region. Furthermore, the values of the content of Mn-Ti. The Curie temperature value was measured using the DC resistivity and Lorria-Sinha methods. The CCNR type of electrical switching was observed in the investigated Cd-Al-Mn ferrites at room temperature. The switching electric field enlarged with the enlargement of the content of Mn-Ti in the ferrite structure. There was no ageing observed in the prepared ferrite system.

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References

 Finch, G. I., Sinha A. P. B., Sinha K. P. (1957) Crystal Distortion in Ferrite-Manganties, Proceedings of the Royal Society of London Series A: Mathematical and Physical Sciences 242: 28-35. https://doi.org/10.1098/rspa.1957.0151



- Dolcet, P., Diodati, S., Zorzi F., Voepel P., Seitz C., Smarsly B. M., Mascotto S., Nestola F., Gross S. (2018) Very fast crystallisation of MFe2O4 spinel ferrites (M = Co, Mn, Ni, Zn) under low temperature hydrothermal conditions: a time-resolved structural investigation, Green Chemistry 20: 2257-2268. https://doi.org/10.1039/C8GC00086G
- 3. Hu, W., Qin, N., Wu, G, Lin, Y., Li, S., Bao, D. (2012) Opportunity of spinel ferrite materials in nonvolatile memory device applications based on their resistive switching performances, Journal of American Chemistry Society 134: 14658-14661. https://doi.org/10.1021/ja305681n
- Ahlawat, A., Satapathy, S., Shirolkar, M. M., Li, J., Khan, A. A, Deshmukh, P., Wang, H., Choudhary, R. J., Karnal, A. K. (2018) Tunable Magnetoelectric Nonvolatile Memory Devices Based on SmFeO3/P(VDF-TrFE) Nanocomposite Films, ACS Applied Nano Materials 1: 3196-3203. https://doi.org/10.1021/acsanm.8b00401
- 5. Hao, A., Ismail, M., He, S., Qin, N., Huang, W., Wu, J., Bao, D. (2018) Improved unipolar resistive switching characteristics of Au-doped nickel ferrite magnetic thin films for nonvolatile memory applications, Journal of Alloys and Compounds 732: 573-584. https://doi.org/10.1016/j.jallcom.2017.10.251
- 6. Kefeni, K. K., Mamba, B. B., Msagati, T. A. M. (2017) Application of spinel ferrite nanoparticles in water and wastewater treatment: a review, Separation and Purification Technology 188: 399-422. https://doi.org/10.1016/j.seppur.2017.07.015
- Amiri, M., Akbari, A., Ahmadi, M., Pardakhti, A., Salavati-Niasari, M. (2017) Synthesis and in vitro evaluation of a novel magnetic drug delivery system; proecological method for the preparation of CoFe2O4 nanostructures, Journal of Molecular Liquids 249: 1151-1160. https://doi.org/10.1016/j.molliq.2017.11.133
- Amiri, M., Salavati-Niasari, M. Pardakhty, A., Ahmadi, M., Akbari, A. (2017) Caffeine: A novel green precursor for synthesis of magnetic CoFe2O4 nanoparticles and pH-sensitive magnetic alginate beads for drug delivery, Materials Science and Engineering C 76: 1085-1093. https://doi.org/10.1016/j.msec.2017.03.208
- Omer, A. M., Tamer, T. M., Khalifa, R. E., Gaber, S. A., Mohy Eldin, M. S. (2019), Smart Biopolymer Hydrogels Developments for Biotechnological Applications. In: Mondal MIH (ed) Cellulose-Based Superabsorbent Hydrogels. Polymers and Polymeric Composites: A Reference Series. Springer Nature, Cham, Switzerland pp 1515-1536. https://doi.org/10.1016/j.msec.2017.03.208
- Mohapatra, S., Rout, S. R., Maiti, S., Maiti, T. K., Panda, A. B. (2011) Monodisperse mesoporous cobalt ferrite nanoparticles: synthesis and application in targeted delivery of antitumor drugs, Journal of Materials Chemistry 21: 9185- 9193. https://doi.org/10.1039/C1JM10732A
- 11. Verma, A., Alam, M. I., Chatterjee, R., Goel, T. C., Mendiratta, R. G. (2005) Development of a New Soft Ferrite Core for Power Applications, Journal of Magnetism and Magnetic Materials 300: 500-501. https://doi.org/10.1016/j.jmmm.2005.05.040
- 12. Manikandan, V., Kim, J. H., Mirzaei, A., Kim, S. S., Vigneselvan, S., Singh, M., Chandrasekaran, J. (2019) Effect of temperature on gas sensing properties of lithium (Li) substituted (NiFe2O4) nickel ferrite thin film, Journal of Molecular Structure 1177: 485-490. https://doi.org/10.1016/j.molstruc.2018.09.085
- 13. Gadkari, A. B., Shinde, T. J., Vasambekar, P. N. (2011) Ferrite Gas Sensors, IEEE Sensors Journal 11: 849-861. https://doi.org/10.1109/JSEN.2010.2068285
- Yang, Y., Li, J., Zhao, J., Chen, J., Gan, G., Wang, G., He, L. (2019) Synthesis of nickel zinc ferrite ceramics on enhancing gyromagnetic properties by a novel low-temperature sintering approach for LTCC applications, Journal of Alloys and Compounds 778: 8-14. https://doi.org/10.1016/j.jallcom.2018.11.144
- Harris, V. G., Geiler, A., Chen, Y., Yoon, S. D., Wu, M., Yang, A., Chen, Z., He, P., Parimi, P. V., Zuo, X., Patton, C. E., Abe, M., Acher, O., Vittoria, C. (2009) Recent advances in processing and applications of microwave ferrites, Journal of Magnetism and Magnetic Materials 321: 2035-2047. https://doi.org/10.1016/j.jmmm.2009.01.004



- Dalawai, S. P., Gadkari, A. B., Shinde, T. J., Vasambekar, P. N. (2013) Effect of sintering temperature on structural and electrical switching properties of Cadmium ferrite, Advanced Materials Letters 4: 586- 590. https://doi.org/10.5185/amlett.2012.10431
- 17. Dalawai, S. P., Gadkari, A. B., Vasambekar, P. N. (2015) Electrical switching in cadmium ferrite with different rare-earth ions (Sm3+, Y3+, and La3+), Rare Metals 34: 133-136. https://doi.org/10.1007/s12598-014-0235-1
- Nazir, M. A., Ul-Islam, M., Ali, I., Ali, H., Ahmad, B., Ramay, S. M., Raza, N., Ehsan, N. M. F., Ashiq, M. N. (2016) Structural, electrical and dielectric properties of multiferroics and spinel ferrite composites, Journal of Electronic Materials 45, 1065-1072. https://doi.org/10.1007/s11664-015-4286-3
- 19. Chavan, A. R., Birajdar, S. D., Chilwar, R. R., Jadhav, K. M. (2018) Structural, morphological, optical, magnetic and electrical properties of Al3+ substituted nickel ferrite thin films, Journal of Alloys and Compounds 735: 2287-2297 (2018). https://doi.org/10.1016/j.jallcom.2017.11.326
- Ahsan, M. Z., and Khan, F. A. (2017) Study of Structural, Electrical and Magnetic Properties of Manganese Doped Cobalt Ferrite Nanoparticles with Non-stoichiometric Composition, Journal of Physical Science and Application 7: 30-37. https://doi.org/10.17265/2159-5348/2017.06.005
- Kim H., Wesstrom, B., Alam, S., Ouchi, T., Azimi, G., Neelameggham, N. R., Wang, S., Guan, X. (2018), Rare Metal Technology 2018. Springer Nature, New York, pp. 5. https://doi.org/10.1007/978-3-319-72350-1
- 22. http://www.chemicool.com/elements/titanium.html
- 23. Mirzaee, O. (2014) Influence of PbO and TiO2 additives on the microstructure development and magnetic properties of Ni–Zn soft ferrites, Journal of King Saud University 26: 152-158. https://doi.org/10.1016/j.jksues.2013.05.005
- 24. Ravinder, D. (2000) Electrical transport properties of cadmium substituted copper ferrites, Materials Letters 43: 129-138. https://doi.org/10.1016/S0167-577X(99)00245-1
- 25. Iyer, R., Desai, R., Upadhyay, R. V. (2009) Low temperature synthesis of nanosized Mn1-xCdxFe2O4 ferrites, Indian Journal of Pure and Applied Physics 47: 180-185.
- 26. Sattar, A. A., El-Sayed, H. M., El-Tabey, M. M. (2005) The effect of Al-substitution on structure and electrical properties of Mn-Ni-Zn ferrites, Journal of Materials Science 40: 4873-4879. https://doi.org/10.1007/s10853-005-3884-5
- 27. Rao, B. P., Rao, K. H., Rao, T. V., Padurarua, A., Caltun, O. F. (2005) DC resistivity and dielectric studies on Ti4+ substituted Ni-Zn ferrites, Journal of Optoelectronics and Advanced Materials 7: 701-704.
- Zuo, X., Barbiellini, B., Vittoriaa, C. (2004) Calculation of exchange constants in manganese ferrite (MnFe2O4), Journal of Magnetism and Magnetic Materials 306: 272-276. https://doi.org/10.1016/j.jmmm.2003.12.466
- 29. Yamashiro, T. (1973) Electrical Switching and Momory Phenomena in CuFe2O4, Japanese Journal of Applied Physics 12: 148-149. https://doi.org/10.1143/JJAP.12.148
- 30. Kamble, P. N., Vaingankar, A. S., Kulkarani, V. R. (1990) Structural and magnetic studies on slow cooled and quenched Cd sub (x) Cu sub (1-x) Fe sub (2) O sub (4) system, Indian Journal of Pure & Applied Physics 28: 542-545.
- Vasambekar, P. N., Kolekar, C. B., Vaingankar, A. S. (1999) Electrical switching in CdxCo1- xFe2yCryO4 system, Materials Research Bulletin 34: 863-868. https://doi.org/10.1016/S0025-5408(99)00081-1
- 32. Saija, K. G., Joshi, U. S., Lakhani, V. K., Modi, K. B. (2009) CCNR type high field instability in Ti4+substituted Mn–Zn ferrites, Journal of Physics D: Applied Physics 42: 165402-165407. https://doi.org/10.1088/0022-3727/42/16/165402
- 33. Patange, S. M., Shirsath, S. E., Jadhav, S. S., Lohar, K. S., Mane, D. R., Jadhav, K. M. (2010) Rietveld refinement and switching properties of Cr3+ substituted NiFe2O4 ferrites, Materials Letters 64: 722-724. https://doi.org/10.1016/j.matlet.2009.12.049
- 34. Patange, S. M., Shirsath, S. E., Lohar, K. S., Jadhav, S. S., Kulkarni, N., Jadhav, K. M. (2010) Electrical and switching properties of NiAlxFe2-xO4 ferrites synthesized by chemical method, Physica B: Condensed Matter 406: 663- 668. https://doi.org/10.1016/j.physb.2010.11.081



- Chhaya, U. V., Mistry, B. V., Bhavsar, K. H., Gadhvi, M. R., Lakhani, V. K., Modi, K. B., Joshi, U. S. (2011) Structural parameters and resistive switching phenomenon study on Cd0.25 Co0.75 Fe2O4 ferrite thin film, Indian Journal of Pure & Applied Physics 49: 833-840.
- Kochmański, M., Paszkiewicz, T., Wolski, S. (2013) Curie–Weiss magnet: a simple model of phase transition, European Journal of Physics 34: 1555–1573. https://doi.org/10.1088/0143-0807/34/6/1555
- Neifel'd, E. A., Arkhipov, V. E., Ugryumova, N. A., Korolev, A. V., Mukovskii, Y. M. (2007) Temperature dependence of the activation energy of manganite conductivity in the paramagnetic phase, Bulletin of the Russian Academy of Sciences: Physics 71: 1559-1560. https://doi.org/10.3103/S1062873807110251
- 38. Loria, K. K. and Sinha, A. P. B. (1963) Curie temperature of magnetic materials using simple equipment, Indian Journal of Pure & Applied Physics 1: 115-165.
- 39. Bhosale, J. L., Kulkarni, S. N., Sasmile, R. B., Chougule, B. K. (1996) Susceptibility and magnetization studies of Gd3+ substituted Mg-Cd ferrites, Bulletin of Materials Science 19: 767-774. https://doi.org/10.1007/BF02745197
- 40. Kadam, G. B., Shelke, S. B., Jadhav, K. M. (2010) Structural and electrical properties of Sm3+ Doped Co- Zn Ferrite, Journal of Electronic and Electrical Engineering 1: 15-25. https://doi.org/10.1016/j.jmmm.2004.05.029
- 41. Zhong, H. and Zhang, H. (2004) Effects of different sintering temperature and Mn content on magnetic properties of NiZn ferrites, Journal of Magnetism and Magnetic Materials 283: 247-250. https://doi.org/10.1016/j.jmmm.2004.05.029
- 42. Standley, K. J. (1990), Oxide Magnetic Materials, Claredon Press, Oxford.
- 43. Dogra, A., Kumar, R., Kumar, N., Sen, P., Singh, M. (2004) Structural and magnetic studies of NiMn0.05TixMgxFe1.95-2xO4 ferrite, Materials Science and Engineering: B 110: 243-250. https://doi.org/10.1016/j.mseb.2004.02.001
- 44. Scherrer, P. (1918) Messages from the Society of Sciences, Gottingen, Journal of Mathematical Physics 2: 98-100.
- 45. Langford JI and Wilson AJC (1978) Scherrer after sixty years A survey and some new results in the determination of crystallite size, Journal of Applied Crystallography 11: 102-113. https://doi.org/10.1107/S0021889878012844
- 46. Smit, J. and Wijn, H. P. J. (1957) Ferrites, Wiley, New York, pp. 233.
- 47. Gadkari, A. B., Shinde, T. J., Vasambekar, P. N. (2011) Synthesis, characterization and magnetic properties of La3+ added Mg–Cd ferrites prepared by oxalate co-precipitation method, Journal of Alloys and Compounds 509: 966-972. https://doi.org/10.1016/j.jallcom.2010.08.155
- 48. Globus, A., Pascard, H., Cagan, V. (1977) Distance between magnetic ions and fundamental properties in ferrites, Journal de Physique Colloques 38: 163-168. https://dx.doi.org/10.1051/jphyscol:1977132
- 49. Lide, D. R. (1995), CRC Handbook of chemistry and Physics, 76th ed. CRC press, London.
- 50. Ghazanfar, U., Siddiqi, S. A., Abbas, G. (2005) Structural analysis of the Mn–Zn ferrites using XRD technique, Materials Science and Engineering B 118: 84-86. https://doi.org/10.1016/j.mseb.2004.12.018
- 51. Shirsath, S. E., Jadhav, S. S., Toksha, B. G., Patange, S. M., Jadhav, K. M. (2011) Influence of Ce4+ ions on the structural and magnetic properties of NiFe2O4, Journal of Applied Physics 110: 013914-013922. https://doi.org/10.1063/1.3603004
- 52. Waldron, R. D. (1955) Infrared Spectra of Ferrites, Physical Review 99: 1727-1735. https://doi.org/10.1103/PhysRev.99.1727
- 53. Ravinder, D. (1999) Far-infrared spectral studies of mixed lithium–zinc ferrites, Materials Letters 40: 205-208. https://doi.org/10.1016/S0167-577X(99)00075-0
- 54. Hemeda, O. M. (2004) IR spectral studies of Co0.6Zn0.4MnxFe2_xO4 ferrites, Journal of Magnetism and Magnetic Materials 281: 36-41. https://doi.org/10.1016/j.jmmm.2004.01.100
- 55. Laidler, K. J. (1987), Chemical Kinetics, 3th Ed, Harper & Row, pp 42.



- 56. Hajalilou, A., Kamari, M. H., Shameli, K. (2017) Dielectric and electrical characteristics of mechanically synthesized Ni-Zn ferrite nanoparticles, Journal of Alloys and Compounds 708: 813-826. https://doi.org/10.1016/j.jallcom.2017.03.030
- 57. Lakshman, A., Rao, P. S. V. S., Rao, B. P., Rao, K. H. (2005) Electrical properties of In3+ and Cr3+ substituted magnesium–manganese ferrites, Journal of Physics D Applied Physics 38: 673-678. https://doi.org/10.1088/0022-3727/38/5/002
- 58. Chaudhuri, S. P., Sarkar, P., Chakraborty, A. K. (1999) Electrical resistivity of porcelain in relation to constitution, Ceramics International 25: 91-99. https://doi.org/10.1016/S0272-8842(98)00006-6
- 59. Ajmal, M. and Maqsood, A. (2007) Influence of zinc substitution on structural and electrical properties of Ni1-xZnxFe2O4 ferrites, Materials Science and Engineering: B 139: 164-170. https://doi.org/10.1016/j.mseb.2007.02.004
- 60. Pandya, M. P., Modi, K. B., Joshi, H. H. (2005) Study of conduction mechanism in aluminium and magnesium co-substituted lithium ferrite, Journal of Materials Science 40: 5223-5232. https://doi.org/10.1007/s10853-005-4416-z
- 61. Yu, H., Kim, M., Kim, Y., Lee, J., Kim, K. K., Choi, S. J., Cho, S. (2014) Al-doped ZnO as a switching layer for transparent bipolar resistive switching memory, Electronic Materials Letters 10: 321-324. https://doi.org/10.1007/s13391-013-3225-9
- 62. Sawa, A. (2008) Resistive switching in transition metal oxides, Materials Today 11: 28-36. https://doi.org/10.1016/S1369-7021(08)70119-6

