

Study of Electrical and Magnetic Properties of Praseodymium Samarium Doped Novel Magnesium Ferrite

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ABSTRACT

The Praseodymium, Samarium doped novel Magnesium ferrite ($Mg Pr_x Sm_y Fe_{2-x-y} O_4$) was prepared by sol gel route and sintered in a microwave furnace. The nano size, structure and composition of Pr and Sm doped Magnesium ferrite ceramics was analyzed by X-ray diffraction and confirmed by SEM monographs. The elemental conformation was done by EDAX. The hysteresis property of this material was conformed through its hysteresis curves. The permeability of this material was calculated by using the magnetic saturation obtained from the hysteresis curves. The electrical measurements have been performed to determine the dielectric constant (ϵ_r), dielectric loss (ϵ_r'') and loss tangent in the frequency range of 20KHz - 20MHz. It is also found that the permittivity of these nano materials is being reduced with the increase in frequency.

Keywords: Pr-Sm doped Mg ferrite; Sol gel, Electrical and Magnetic studied Studies

1. INTRODUCTION

Ferrites are ferrimagnetic materials that are particularly attractive at microwave frequencies because they do not obey the reciprocity principle, and can control relatively high powers. Ferrites are polycrystalline (and sometimes single crystal) ceramic materials that are typically formed using a high temperature sintering process [1,4]. They exhibit dielectric behavior with high resistivity and low dielectric losses and are widely used in microwave and millimeter wave applications such as inductors, circulators, isolators, phase shifters, switches, tunable resonators and filters [5]. Metallic magnetic alloys are ferromagnetic materials, with very high magnetization compared to ferrites another attractive feature is that they typically have low coercivities, allowing them to be utilized without need of an external magnetic bias field to saturate the sample, meaning that they are self-biased. They are metallic in nature, so have lower resistivity (than ferrites) and suffer from conductive losses such as skin effect and eddy currents. This severely limits their applications to $RF < 1GHz$. However, these materials can be deposited using a low temperature RF sputtering process, making them compatible to semiconductor fabrication. A common application of metallic magnetic alloy is RF planar inductors [6,7].

The co-existence of ferro electricity and ferromagnetism and their coupling with elasticity provide an extra degree of freedom in the design of new functional sensors and multistate devices.

Due to its multiferroism, an electric field can induce change in magnetization and an external magnetic field can induce electric polarization. This phenomenon is known as the magneto electric effect (ME) effect and materials exhibiting this effect are called magneto electric or signets magnets. Further proof of it being ferromagnetic is that it produces a hysteresis loop during ferroelectric characterization. The ability to couple to either the electric or the magnetic polarization allows an additional degree of freedom in device designs.

One of the major drawbacks of $MgFe_2O_4$ material is the leakage current arising out of its non stoichiometry. This is mostly because of the difficulty in obtaining stoichiometric single phase $MgFe_2O_4$ materials. Therefore it allows current to pass through when a high voltage is applied. Attempts to improve the electrical properties have been made by doping it with rare earth elements such as Lanthanum (La), Praseodymium (Pr), Samarium (Sm), Gadolinium (Gd), Terbium (Tb) and Cerium (Ce), Dysprosium (Dy) etc. The dopant can be at the A site or the B site. A site being the edges of the perovskite cell and the B site being the centre of the perovskite cell.

2. EXPERIMENTAL PROCEDURE

2.1 Synthesis Technique:

The nano sized Magnesium ferrite doped with different concentration of Praseodymium (Pr) and Samarium(Sm) is prepared by using Magnesium Nitrate (Merck) and ferric(Lobo Chem) and rare earth Ce(Alfa Aesar), along with citric acid(Merck) in a certain molar ratio of 1:1 and then dissolved in deionized water, here the citric acid helps the homogenous distribution of the metal ions to get segregate from the solutions. Further a required amount of ammonia is added in order to adjust the pH value to about 7, since the base catalysts are employed in order to speed up the reaction. The solution is later subjected to a continuous stirring for duration of 24 hrs. This as prepared solution is heated to a constant temperature of 135°C to condense it into a xerogel [8-9]. After this dehydration process a brown colored dried gel is obtained. The burnt powder is further crushed in agate mortar to obtain the nano sized powder. Further the powder is subjected to sintering in a microwave furnace.

The grain size of the nanoferrite is determined from the prominent peak of XRD using Scherer's equation. Using the knowledge of site preference of the ions and the ionic size data of the respective ions, the cation distribution has been estimated

theoretically using the formula as proposed [10, 11]. These nano ferrites possess a very well defined local atomic ordering that may be described in terms of a spinel-type structure with Mg^{2+} and Fe^{3+} ions which is almost randomly distributed over its tetrahedral and octahedral sites. The new structural information helps to explain the material's unusual magnetic properties [12]. The experimental magnetic moment is calculated from the following formula [13].

$$\eta = \frac{[M_W * M_S]}{5585}$$

Where M_W is the molecular weight of the sample and M_S is the saturation magnetization in emu/g.

2.2 XRD and EDX Studies

The phase composition of fine ferrite powder is carried out using PAN analytical X'pert PRO diffraction meter using $Cu K_{\alpha}$ radiation ($\lambda=1.54\text{\AA}$) at 40KV and 30mA with a scanning rate of $0.01^\circ/s$ and scan speed of $1^\circ/min$ in a 2θ range of $10-80^\circ A$. The crystallite size is calculated by taking RWHM of the 1,1,1 peak in XRD and using the Scherrer formula. The energy dispersive studies (EDAX) are done on Genesis EDAX to confirm the presence of chemical composition of the powder and to study the structure of the powdered material and the presence of the elements.

2.3 SEM Studies

SEM Micrographs of the nanoferrite powder are recorded using the scanning electron microscope (HITACHI model S-3000H).

2.4 Magnetic Measurements

The Magnetic measurements are performed on the commercial vibrating sample magnetometer (VSM) Lakeshore (Model73009). The Magnetic hysteresis loops are measured at the room temperature with maximal applied magnetic fields up to 0.95T. Magnetic field sweep rate is kept at 5 Oe/s for all the measurements, so that the measurement of hysteresis loops with maximum field of 0.989 T is taken from an interval of three hours. The saturation magnetization, coercivity and remanent magnetization are found from hysteresis loop.

2.5 Electrical Measurements

The Electrical measurements are performed using the N4L LCR meter. The experimental set up for measuring the dielectric properties in the microwave region consisted of a pallet holder connected to the N4L LCR meter interfacing the computer. The microwave properties of the four samples $Pr(x) Sm(y)$ doped Magnesium ferrite $x = 0.05, 0.06, 0.07$ $y = 0.03$ are investigated at the frequency range from 20 KHz to 20 MHz. The electrical conduction mechanism can be explained by the electron hopping model of Heikes and Johnston [17].

3.0 RESULT AND DISCUSSION:

3.1 X-RAY DIFFRACTION

A careful analysis of the XRD patterns helps to determine the respective planes and face centered cubic structure of these ferrites. Well resolved peaks in XRD pattern clearly indicates the single phase and polycrystalline nature of the samples.

Figure 1 shows XRD patterns of the $Mg Pr_x Sm_y Fe_{2-x-y} O_4$ powders. The diffraction patterns and relative intensities of all diffraction peaks are matched well with those of JCPDS card 22-1086 for $Co_{0.5}Zn_{0.5}Fe_2O_4$ and the Ce diffraction peaks are matched well with those of JCPDS card 34-0394. The peaks are appeared at around $18.5^\circ, 30.2^\circ, 35.6^\circ, 37.2^\circ$ and 43.0° for Co and Ce, 53.4° for Ce and $57.1^\circ, 62.5^\circ$ and 73.7° appeared for Co. These peaks are well indexed to the crystal plane of spinel ferrite (111), (220), (311), (222), (400), (422), (511), (440) and (533), respectively. The diffraction peaks are quite sharp because of the micrometer size of the crystallite. XRD patterns clearly indicate that the pure Lanthanides doped $MgFe_2O_4$ shows the presence of single-phase cubic spinel structure. The X-ray diffraction patterns show that all samples are formed in cubic single spinel phase. No foreign impurity lines are seen. The lattice parameter a (\AA) is calculated using Bragg's law.

Where h, k, l are the indices of mentioned planes. Lattice constants of all samples that are prepared in investigation are listed in Table 1. The lattice constants of individual phases do not vary much by the inclusion of Pr-Sm and it was found that the porosity and density had shown an increase with increase in Pr-Sm doping concentration.

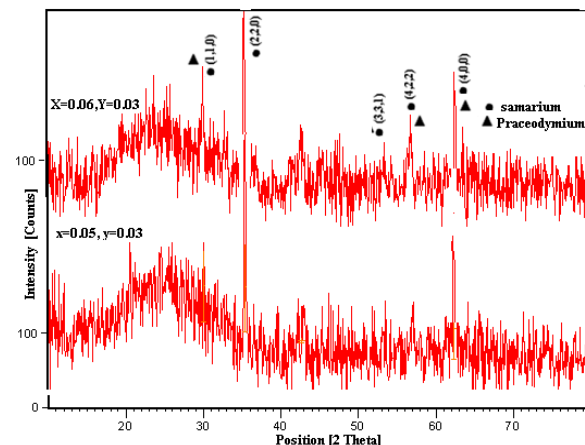


Fig1 XRD patterns of sintered $Mg Pr_x Sm_y Fe_{2-x-y} O_4$ $x=0.05$ and $y=0.03$

The size of crystal is evaluated by measuring the FWHM of the most intense peak (311) from XRD and by using the Debye Scherrer's formula [14], the size of the crystal is evaluated.

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

Here the XRD patterns exhibit narrow reflection that points out the narrow size crystallites. The mean crystallite size of the sample lies within the range of 41.52 nm to 54.79 nm. The lattice parameter increased with increasing the doping concentration.

Table 1 Lattice parameter (*a*), crystallite size (*D*), X-ray density (*d_x*), porosity (*p*) and observed molar contents of Mg Pr_xSm_yFe_{2-x-y}O₄

Zn _{1-x-y} Ce _x Co _y Fe ₂ O ₄	x=0.05 y=0.03	x=0.06 y=0.03	x=0.08 y=0.04	x=0.09 y=0.05
a(A°)	8.145	8.196	8.23	8.36
D(nm)	41.52	43.62	48.21	54.79
d _x × 10 ³ gcm ⁻³	3.456	3.687	3.948	4.239
<i>p</i>	0.321	0.315	0.304	0.298
Observed contents (Pr)	0.05	0.06	0.08	0.09
Observed Contents (Sm)	0.03	0.03	0.04	0.05

It is also seen that the density of magnesium ferrite increased with the doping concentration of Pr³⁺-Sm²⁺ shown in Fig.3(b), it is because the molecular weight of the Praseodymium (140.902 amu) and Samarium (150.36 amu) are higher than the molecular weight of Fe (55.845 amu), so when the Pr and Sm are replaced by Fe, and therefore the density increases). The percentage of porosity in Dy-Sm doped magnesium ferrite was decreased from 0.321 to 0.298 with respect to the increasing doping concentration

3.2 EDAX

The EDAX spectra obtained from the center of Mg substituted Pr-Sm ferrite grains indicated the presence of small concentration of Mg inside the grains Maximum of 567 counts was seen for Fe at 6.3 Kev and 7.0 Kev Whereas for Mg it was 252 counts at 1.2 Kev, Whereas for Samarium it was 239 and 220 having the percentage 5 at 5 Kev to 7 Kev, Whereas for Praseodymium it was seen at 4.5 to 6.5 Kev.

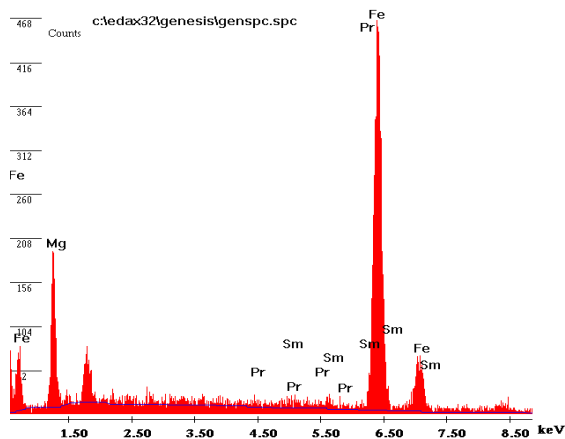


Fig.2 EDAX pattern for Mg Pr_x Sm_y Fe_{2-x-y} O₄ x=0.05,0.03

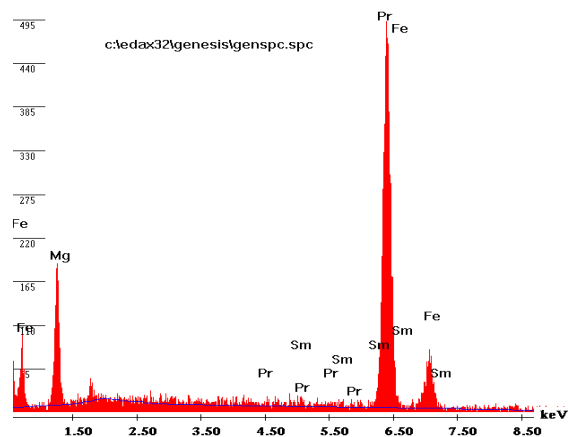


Fig.3 EDAX pattern for Mg Pr_x Sm_y Fe_{2-x-y} O₄ x=0.06,0.03

3.3 SEM analysis

The nano phase is investigated by using the SEM micrograph, as shown in Fig. they show the microstructure of the sintered specimen. These Ce-doped specimens show a bi-phasic microstructure constituted of dark ferrite matrix grains and small whitish grain at the grain junction/boundary. As proposed by Sattar et, al [15] the rare earth ions occupy either the iron positions or go to the grain boundaries. However, we have to exclude the probability that the rare earth ions occupy the A site of Fe³⁺ ions. This is due to the fact that the tetrahedral sites are small to be occupied by the large rare earth ions which have large ionic radius.

Of course the probability of occupancy of the octahedral (B-site) is by the rare earth ions (Ce). With the increase in Ce ions the ionic radius R decreases. This is indicated by the whitish grains of Ce-Co with Fe₂O₄. The amount of Pr-Sm with Fe₂O₄ is maximum in x = 0.016 composition. The grain size of matrix phase is also maximum in x = 0.016 composition. Relatively lower grain size of ferrite matrix is seen in x= 0.012 compositions, it may be due to the grain growth inhibition caused by Ce Fe₂O₄.

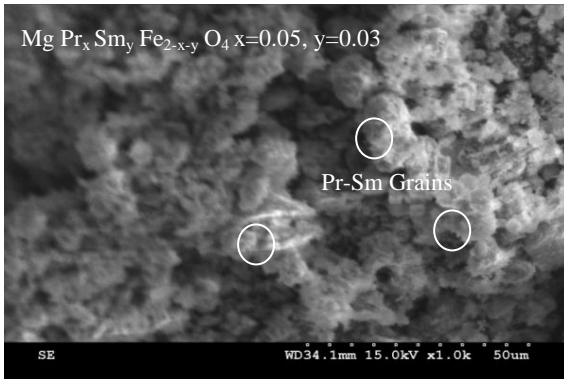


Fig.4 $Zn_{1-x-y}Ce_xCo_yFe_2O_4$ $x=0.05, y=0.03$

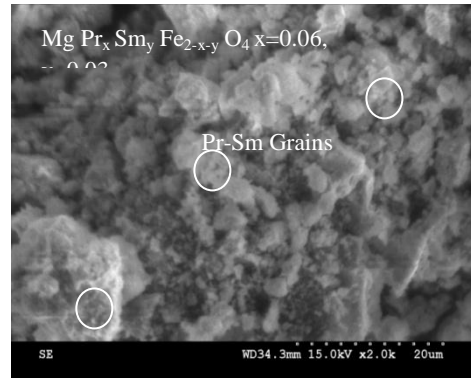


Fig.5 $Zn_{1-x-y}Ce_xCo_yFe_2O_4$ $x=0.06, y=0.03$

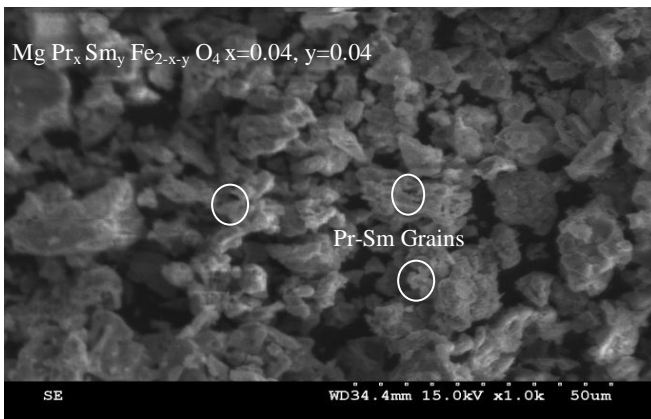


Fig.6 $Mg Pr_x Sm_y Fe_{2-x-y} O_4$ $x=0.08, y=0.04$

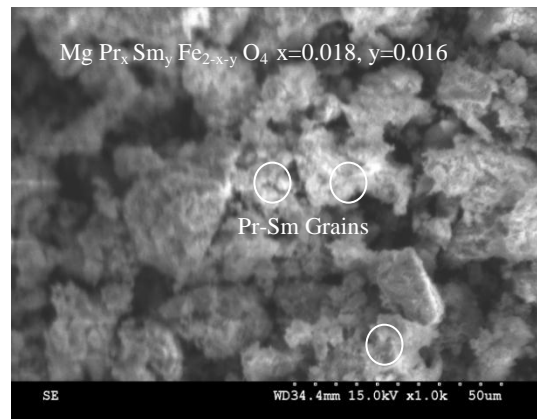


Fig.7 $Mg Pr_x Sm_y Fe_{2-x-y} O_4$ $x=0.09, y=0.05$

3.5 Hysteresis studies:

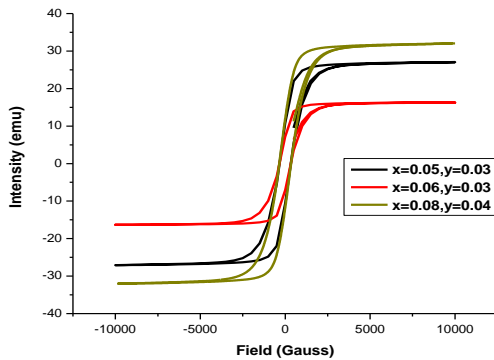
Table 2 The change in magnetic saturation, retentivity, coercive force with changes in Pr-Sm doping concentration

S.N	Material $Mg Pr_x Sm_y Fe_{2-x-y} O_4$		Coercivity (G)	Remanance (emu/g)		Saturation Magnetization (emu/g)		Retentivity (emu/g)
	x	y		Positive	Negative	Positive	Negative	
1	0.05	0.03	345.62	11.181	-11.039	15.383	-25.680	11.110
2	0.06	0.03	349.61	6.4113	-6.3726	25.673	-15.350	6.3919
3	0.08	0.04	346.79	13.809	-13.719	31.517	-31.506	13.764

The different parameters such as saturation magnetization (M_C), coercive force (H_C), and Retentivity, The dielectric constant ϵ_r and dielectric loss ϵ_r' are listed in Table 3. The magnetic properties have been seen to be altered by the addition of Pr and Sm in Mg ferrite, It is observed that the saturation

magnetization increases with the addition of Pr and Sm. Rezlescu et al. [16], the saturation magnetization of Pr^{3+} and Sm^{3+} is substituted in Magnesium ferrites is higher than that of un substituted ferrite. Similar results are reported by Liu et al. [17] in Pr^{3+} and Sm^{3+} substituted M-type Cerium ferrite and similar results is reported by Gama et al is seen in cerium-doped Zn ferrite [18].

Fig.8 Magnetic hysteresis loop for Dy-Sm doped Mg ferrite



Therefore 3.8 is observed for the sample $Zn_{0.978}Ce_{0.012}Co_{0.01}Fe_2O_4$ and minimum is 0.645 for the sample $Zn_{0.985}Ce_{0.014}Co_{0.001}Fe_2O_4$, as mentioned in table 3. These values are attributed to better concentration and nature of the ions in A and B site causes resultant magnetization to be different as reported.

The effect of grain size on initial permeability and found a linear relation between the initial permeability and grain size in Pr-Sm doped magnesium ferrite. The relationship between μ_i , saturation magnetization M_s and grain size D can be expressed as [19,20]

$$\mu_i = M_s^2 D / K_1$$

where M_s is the saturation magnetization, D the average grain size and K_1 is the magneto-crystalline anisotropy constant. The relation between μ_i with M_s and D for the Pr doped nano ceramic magnesium ferrites show the agreement with the Eq.(5)

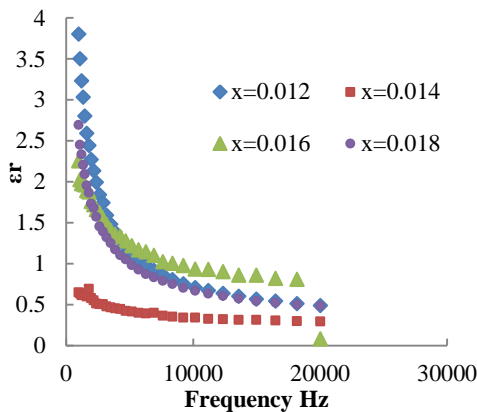


Fig9.Dielectric constant for Mg Pr_xSm_yFe_{2-x-y}O₄

4. CONCLUSION:

The dielectric constant ϵ_r and the dielectric loss ϵ_r' decrease with increasing frequency for all Praseodymium, Samarium doped ferrites. This behavior of a dielectric is explained qualitatively in terms of the supposition that the process of dielectric polarization takes place through a mechanism similar to the conduction process. The increase in the electrical conductivity at

relationship as shown in Fig 7(a) and 7(b), that is $\mu_i \propto M_s$ and $\mu_i \propto D$ [21].

$$K_1 = \frac{M_s H_c}{0.96}$$

3.6 Electrical Properties

The dielectric constant ϵ_r and dielectric loss ϵ_r' of the sintered samples $Mg Pr_x Sm_y Fe_{2-x-y} O_4$, over the microwave frequency range from 10M–20GHz are shown in figure 10 and 11. The plots 11,12 show that the ϵ_r and ϵ_r' values tend to decrease exponentially, it is also seen that the value of ϵ_r and study. The maximum value of dielectric constant compositional stoichiometry single phase spinal structure and uniform microstructure of the sample. The general trend for all composition is that ϵ' and ϵ'' decrease with increasing frequency[22]. single phase spinal structure and uniform microstructure of the sample. The general trend for all composition is that ϵ' and ϵ'' decrease with increasing frequency.

This behavior of a dielectric may be explained qualitatively by the supposition that the mechanism of the polarization process in ferrite is similar to that the conduction process. e_2O_4 , as mentioned in table 3..These values are attributed to better compositional stoichiometry single phase spinal structure and uniform microstructure of the sample. The general trend for all composition is that ϵ' and ϵ'' decrease with increasing frequency. This behavior of a dielectric may be explained qualitatively by the supposition that the mechanism of the polarization process in ferrite is similar to that the conduction process. The electrical conduction mechanism can be explained by the electron hopping model of Heikes and Johnston [23]. It is known that the effect of polarization is to reduce the field inside the medium. Therefore, the dielectric constant of a substance may be decreased substantially as the frequency is increased.

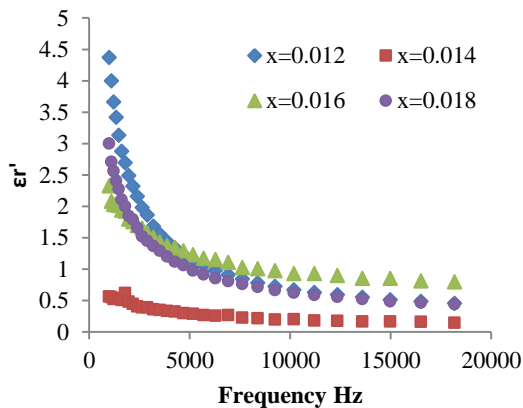


Fig 10. Dielectric loss for Mg Pr_xSm_yFe_{2-x-y}O₄

low temperature is attributed to the impurities, which reside at the grain boundaries. It is seen that the value of ϵ_r and ϵ_r' increases with the addition of Pr and Sm atom concentration, while the capacitance value remains fairly constant for this range of frequency. This investigation also indicates that the addition of Praseodymium and Samarium in zinc ferrite showed a small change in magnetic properties. It is expected that a large concentration of Praseodymium and Samarium may cause a

significant structural change which in turn may enhance the magnetic properties [24-25].

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