



EFFECT OF AL SUBSTITUENT ON STRUCTURAL AND ELECTRICAL PROPERTIES OF VANADIUM YIG

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Abstract:

Substituted YIG with chemical formula $Y_{2-x}Bi_xCaFe_{4.5-y}Al_yV_{0.5}O_{12}$, ($X=0.5, 1.0$ and $Y=1.0, 1.5$) were prepared by standard ceramic technique and characterized by X-ray diffractometry. Analysis of XRD revealed the presence of single crystalline phase with a space group Ia3d. The temperature variation of molar magnetic susceptibility was studied from room temperature to 800K. Most of the samples were found to be ferromagnetic with high Curie temperature and can be explained well. The variation of DC magnetic susceptibility and dielectric constant with temperature from room temperature to 700K was also studied. For the composition $x=1.0$ and $y=1.0$; 1.5 the activation energy of conduction was found low as compared to the composition $x=1.0$ and $y=1.0$; 1.5. The dielectric constant was found to increase rapidly with temperature from 420K to 600K.

Keywords: Garnet; magnetic susceptibility; electrical conductivity; dielectric constant.

Introduction:

In recent years Yttrium-ion garnet (YIG) and its substitutions have attracted many research workers due to their interestingly important applications in industry and technology. Amongst substituted YIG, bismuth-vanadate garnets have narrow resonance line width and are used in microwave (Goernert et al 1986), Magneto optical recording (Orkuda et al 1991), Solid state electronics (Bouwens 1987) and magnetic (Crangle 1977) devices.

Garnets have general chemical formula $\{X_3\} (Z_3) O_{12}$, where the cations X occupy the dodecahedral (c) sites with eight surrounding oxygens, while Y and Z occupy the octahedral (a) and tetrahedral (d) sites with six and four surrounding oxygens respectively (Rotman and Tuller 1987). The cubic unit cell of the garnet contains eight molecules and belongs to the space group Ia3d (O_h^{10-230}). The oxygen atoms occupy general h positions characterized by three positional parameters x, y and z (Geller et al 1987). The point symmetries of the c, a, d and h sites are $222(D_2)$, $3(C_2)$, $4(S_4)$ AND $1(C_1)$ respectively (International Tables for X-ray Crystallography (1967)).

Ferrimagnetic garnets containing V^{+5} in combination with Ca^{+2} for electrostatic compensation have been reported by Geller et al (1963). The substitution of Bi^{+3} reduces the preparation temperature of the polycrystalline iron garnets and Al^{+3} substituted iron garnets. The V^{+5} ions having no site preference energy, occupy d-sites, Ca^{+2} and Bi^{+3} along with Y^{+3} occupy the c-sites (Chatterjee et al 1978), while substitution of Al^{+3} ions for Fe^{+3} ions in YIG prefers tetrahedral d-sites. However, it has been observed that V^{+5} , Al^{+3} and Fe^{+3} ions distribute themselves in both octahedral and

tetrahedral sites (Geller et al 1964; Rotman and Tuller 1987) cation ordering between Fe^{+3} and Al^{+3} has been reported previously to be present on a large scale in a silicate garnet giving rise to optical birefringence and reduction in symmetry from a cubic to an orthorhombic space group (Takeuchi and Haga 1976). Furthermore cation redistribution of Fe^{+3} and Al^{+3} over the octahedral and tetrahedral sites is known to affect the magnetic, electrical, dielectric and other properties of the ferrite garnets [13] (Roschmann 1981).

The effect of substitution and distribution of the cations at different sites on the magnetic, electrical transport properties and kinetic of the synthetic garnet (Balestrino and Geller, Rotman and Tuller 1990, Shanon et al 1991, Salem and Elshereafy 1994) have been examined as they give information about the structure and other physical properties. Present study deals with the same combined effect of partial substitution of nonmagnetic V^{+5} and Al^{+3} for Fe^{+3} ions in a and d-sites, and Ca^{+2} and Bi^{+3} in c-sites of the YIG.

Experimental details:

Sample preparation.

Solid solution of the vanadium substituted YIG with composition $Y_{2-x}Bi_xCaFe_{4-y}Al_yV_{0.5}O_{12}$, ($x = 0.5, 1.0$ and $y=1.0, 1.5$) were prepared using solid state diffusion technique at atmospheric pressure (Hellstrom et al 1989). AR grade oxides, Y_2O_3 , Bi_2O_3 , CaO , V_2O_5 and Fe_2O_3 were mixed intimately in appropriate stoichiometric proportions and ground using AR grade acetone in an agate mortar. The mixture of the fine powder was heated in air at the sintering temperature at 1000°C (Chatterjee et al 1978) for 60 hours in a muffle furnace and then cooled down at the rate of 800°C/hour to room

temperature. The polycrystalline sample thus formed was then ground for about half an hour for experimental investigation (Standley 1972).

X-ray diffraction analysis.

X-ray diffraction pattern (XRD) for all the samples were recorded using Philips X-ray diffractometer with Cu-K α radiation. XRD pattern of the sample showed a presence of single crystalline phase (Petrov et al 1987). The pattern was analysed (Henry et al 1953) assuming the well settled space group Ia3d in which garnets are found (JCPDS-ICDD-1990). Figure 1 shows a typical XRD pattern of the garnet. Y Bi Ca_{0.5} Al V_{0.5} O₁₂. The Lattice parameter and X-ray density of the specimen are included in the table.1

DC electrical conductivity:

The temperature dependence of the DC electrical conductivity was carried out from room temperature to 700K by hot probe technique (Ramasasthy et al 1971). For this the powder specimens were pelletized (1.258 cm in diameter and about 0.2 cm thickness) at pressure of 5 tons per square cm using a

Table -1

Y_{2-x} Ca_{0.5} Fe_{4-y} Al_y V_{0.5} O₁₂

S.No	Sample		Lattice parameter a(AU)	X-ray density d _x (gm/cc)	Activation Energy Ea (eV)	Dc Conductivity at 300k (ohm ⁻¹ cm ⁻¹)
	x	y				
1.	1.0	1.0	12.342	5.498	0.825	-4.309 x10 ⁻¹²
2.	1.0	1.5	12.327	5.416	0.845	-9.261 x 10 ⁻¹²
3.	0.5	1.0	12.337	5.080	0.424	-3.345 x 10 ⁻⁸
4.	0.5	1.5	12.272	5.058	0.574	-1.401x 10 ⁻¹¹

X-ray diffraction pattern of compound Y₁ Ca_{0.5} Fe₃ Al₁ V_{0.5} O₁₂

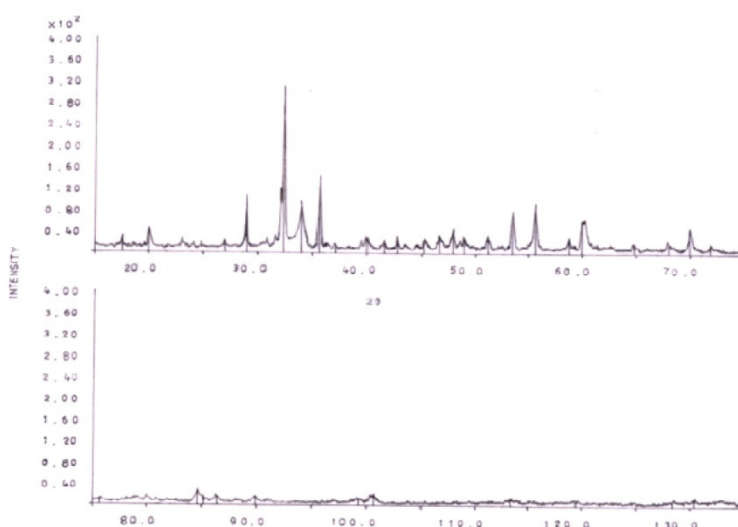


Figure. 1 : X-ray diffraction pattern of compound Y₁ Ca_{0.5} Fe₃ Al₁ V_{0.5} O₁₂

hydraulic press. These prepared pellets were heated in a ceramic boat at 600°C for 3 hours and then cooled down to room temperature before the measurements of the conductivity. The opposite faces of the crack free and flat test pellets were coated with uniform thin layer of air-drying silver paste to ensure good electrical contacts with the brass electrodes. The variation of the DC electrical conductivity lnσ_{dc} with the reciprocal of the temperature 10⁻³/T K⁻¹ is shown in figure 2.

Dielectric Constant:

The dielectric constant ε' as a function of temperature of the compositions were measured at frequency 1KHz from room temperature to 700K using parallel plate capacitance technique (Shanon et al 1991) by digital LCR meter (Model VLCR-17). The pellets of the polycrystalline powder sample prepared for DC electrical conductivity were used for this purpose. The value of ε' were calculated without edge corrections. Figure -3 shows variation of ε' with temperature T.

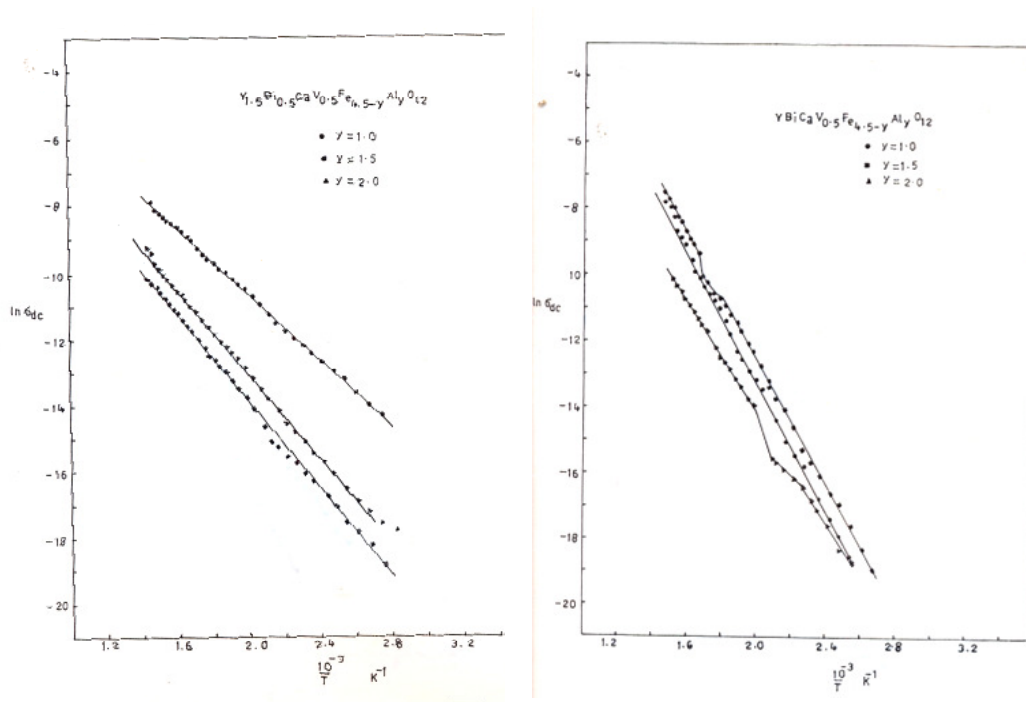


Figure 2: For Electrical Conductivity $\ln \sigma$ verses $1/T \times 10^{-3} \text{ K}^{-1}$

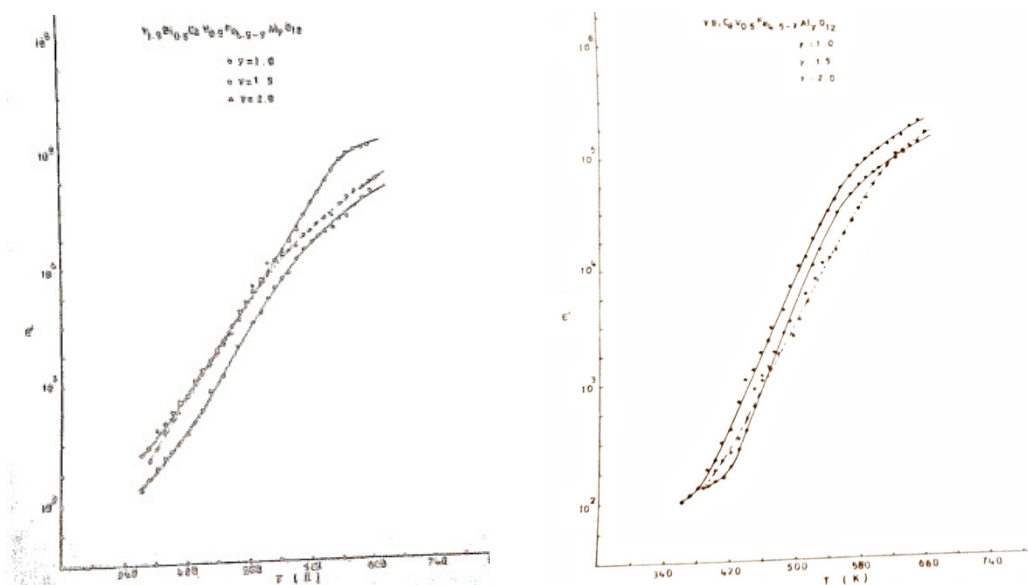


Figure 3 : Plot of dielectric constant ϵ' verses temperature T.

Result and Discussion:

The lattice parameter of $\text{Y}_3\text{FeO}_{12}$ and $\text{Y}_3\text{Al}_5\text{O}_{12}$ is 12.3774 AU and 12.0089 AU respectively (JCPDS-ICDD-1990). The lattice constant and X-ray density of the present series of sample (table 1) lies between the YIG and YAG. The size of the Al^{+3} (0.535 AU) and V^{+5} (0.54 AU) is smaller than Fe^{+3} (0.665 AU high spin state), while size of Bi^{+3} (1.03AU) is slightly more than Ca^{+2} (1.00AU) and Y^{+3} (0.90 AU)) (Shannon 1976). The Bi^{+3} ion in eight-fold coordinated c-sites increases the size of the unit

cell of the garnet, but the substitution and distribution of Al^{+3} for Fe^{+3} by large amount in d-site than in a-site of YIG reduces the unit cell size (Langley et al 1979; Geller et.al 1964). Therefore it was expected to compensate the ionic sizes and do not affect large the size of the unit cell of the newly prepared garnets. The unit cell size are found to be closed to YIG itself. The trend of the decrease of the lattice parameter on substitution of Al^{+3} and V^{+5} for Fe^{+3} in the substituted YIG is found to be in agree with the results of Geller et al (1964).

From the plot of $\ln \sigma_{dc}$ versus $10^{-3}/T$ K⁻¹, the value of activation energy (E_a) of dc conduction were calculated and are listed in table 1. It is known that pure YIG is an ionic crystal having room temperature conductivity below 10^{-3} ohm⁻¹cm⁻¹ (Hartmann et al 1984) and substituted YAG show a mixed ionic-electronic conductivity (Rotman and Tuller 1987). In the present work, the curves are slightly distorted hear to the ferromagnetic curie temperature expect the sample 3. The activation energy is found to rise by increasing Al³⁺ for Fe³⁺ or by reducing the concentration of Bi³⁺ by Y³⁺, by 50%, there is approximately same reduction in the activation energy. This could be attributed to a presence of transition metal ions in two or three sub lattices which forms an extra complications for the explanation of the conductivity (Metselaar and Larsen 1987). In the vanadium garnets, there may be columbic effect interaction which dominate the charge transport behavior (Oversluizen et al 1985).

Figure- 3 shows variation of dielectric constant (ϵ') with temperature T (K). For the series of sample the variation in dielectric constant for temperature lower than 420K is low, beyond this temperature there is rapid increases of the ϵ' upto 600K and further increases in temperature, increases of ϵ' is low. This behavior of the temperature depended of the dielectric constant is similar to the hexaferrites observed by [32] Haberay 1968.

Conclusion:

The samples of vanadium YIG with composition of aluminium were prepared using solid-state diffusion technique. XRD pattern of the sample showed a single crystalline phase with a space group Ia3d in which garnets are found. The lattice parameter decrease by the substitution of Al³⁺ and V⁵⁺ for Fe³⁺ in a YIG. Electrical conductivity of pure YIG is an ionic crystal having room temperature is below 10^{-3} ohm⁻¹cm⁻¹ and substituted YIG show a mixed ionic-electronic conductivity. The activation energy is found to rise by increasing Al³⁺ for Fe³⁺. The temperature depended of the dielectric constant are behaves similar to the hexaferrites materials.

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