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Study of electrical conductivity of gadolinium gallium garnet single crystals

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The electrical conductivity of gadolinium gallium garnet single crystals was measured as a function of temperature and following ambient atmospheres : air, N_2, argon and vacuum (10^{-2} Torr). The room temperature conductivity in air is observed to depend upon the thermal history of the sample. On leaving the sample exposed to air for 12 hours or more at room temperature the electrical conductivity is of the order of $10^{-10}\ \Omega^{-1}\ cm^{-1}$. After heating the sample at 500°C or more in air the value of the electrical conductivity at room temperature is about $10^{-12}\ \Omega^{-1}\ cm^{-1}$. Electrical conductivity σ versus $1/T$ curves obtained with a sample which has been given heat treatment mentioned above can be divided into two regions, when measurements are made under air, N_2 and argon. At lower temperatures (room temperature to $\sim$150°C) the conductivity is found to decrease with increase in temperature. In the higher temperature region the conductivity increases with increase in temperature. The electrical conductivity plot consists of two straight lines with activation energy, $E(I) = 1{\cdot}76$ eV and $E(II) = 1{\cdot}52$ eV in the temperature regions 250–400°C and 400–500°C, respectively in air ambient atmosphere. The results of measurements of electrical conductivity under vacuum are different from the results described above for measurements made under air, N_2 and argon. The conductivity is not found to decrease with increase in temperature in any temperature region. The electrical conductivity plot consists of four straight lines with values of activation energy $E(I) = 1{\cdot}85$ eV, $E(II) = 1{\cdot}31$ eV, $E(III) = 1{\cdot}70$ eV and $E(IV) = 1{\cdot}38$ eV in the temperature regions 220–280°C, 280–320°C, 320–405°C and 405–600°C, respectively. If no heat treatment is given to the sample the conductivity plots are different in heating and cooling cycles. This hysteresis like behaviour disappears after the first heating and cooling cycles.

1. Introduction

Garnets have proved to be of great importance in the field of devices like magnetic bubble memories (Gianola *et al* 1969) and lasers (Geusic *et al* 1964). Nonmagnetic garnets, particularly, gadolinium gallium garnet (GGG) have been extensively used as substrate materials in magnetic bubble memory devices. Although considerable amount of work has been reported on the growth of single crystals (O'Kane *et al* 1973) of these materials and study of their crystal perfection (Mathews *et al* 1973, Stacy *et al* 1974, Krishan Lal & Mader 1976) but very little

has been reported on the study of their properties. In an attempt to understand the physical properties of GGG, we have studied dielectric properties (Krishan Lal & Jhans 1977) and electrical conductivity of GGG. Thermal history and ambient atmosphere during measurement has spectacular effect on the electrical conductivity even at room temperature. Therefore, we have studied the effect of ambient atmosphere and thermal history of the sample on its electrical conductivity. Some results of these investigations are reported in this paper

2. Experimental

GGG single crystals used in this investigation are grown from melt by Czochralski method. These were obtained by one of the authors (Krishan Lal) by courtesy of IBM, Thomas J Watson Research Centre, N.Y Measurements were carried out along [111] direction on (111) disc shaped wafers Platinum electrodes are coated on the two faces of the sample using the Englehard platinum paint and heating the sample at 700°C for 10 minutes

The sample holder used in these investigations is the same as described earlier (Lal & Pahwa 1971) This sample holder permits the measurements under any desired gas or vacuum at or above room temperature

The electrical conductivity of GGG single crystals is of the order of $10^{-16}\ \Omega^{-1}\ cm^{-1}$ at room temperature which cannot be measured accurately. Therefore, electrical conductivity of GGG single crystals was studied from about 500°K to about 900°K. Effect of ambient atmosphere, viz. vacuum (10^{-2} Torr), air, nitrogen and argon on electrical conductivity was also studied

3 Results

Resistance, R, of the samples was measured as a function of temperature, T (°K), both when the temperature of the sample was increasing (room temperature to higher temperatures) and when the temperature of the sample was decreasing (higher temperature to room temperature). Figure 1 shows typical log $1/R$ versus $1/T$ curves for experimental data recorded in heating and cooling cycles Curve 1 is obtained when the sample is heated from room temperature to 900°K (first heating cycle) The sample was cooled from 900°K to room temperature and measurements made in the cooling cycle (first cooling cycle) are plotted as curve 2 To see the effect of thermal history of the sample, measurements were again made as the sample was heated to 900°K and from this temperature it was cooled to room temperature In the second heating and cooling cycles the experimental data points were found to approximately fall on the second heating cycle. Therefore, this has not been plotted as a separate curve

Curve I consists of four straight lines with different slopes. The temperature regions of these straight lines are 490–553°K (I), 553–593°K (II), 593–678°K

(III) and 678–900°K (IV). As is obvious the different curves obey Arrhenius relation, $\sigma \propto e^{-E/kT}$. The value of activation energy, E, was determined from the slopes of these curves The values of activation energy, E, for different curves are, $E(I) = 1{\cdot}85$ eV, $E(II) = 1{\cdot}31$ eV, $E(III) = 1{\cdot}70$ eV and $E(IV) = 1{\cdot}38$ eV in the temperature regions I, II, III and IV, respectively

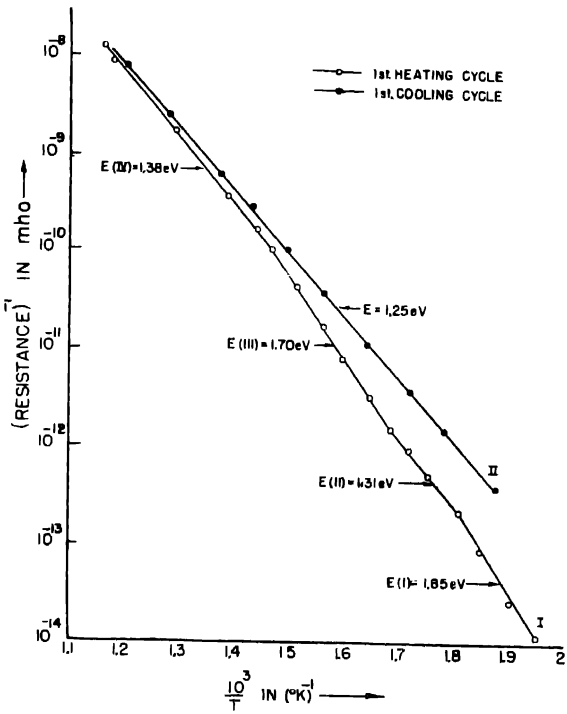

Fig. 1. Two typical log $1/R$ versus $1/T$ curves during heating and cooling cycles for GGG in vacuum

Hysteresis is observed in the heating and cooling curves (Curves I & II of figure 1) Resistivity is higher during heating cycle than during cooling cycle. In curve 2 and subsequent heating and cooling cycles the conductivity plot is a single straight line. The slope of this line gives an activation energy value 1·25 eV

In another experiment while cooling the sample the sample was held at 623°K for about five hours. The conductivity of the sample showed no chan

with time This was done to study the kinetics of transition from the state of *sample after first heating cycle to the state of sample before it. Moreover, it also provided information whether below the apparent knee temperature (678°K in curve I. figure 1) the charge carriers were at equilibrium or not. The result of this experiment shows that the charge carriers are at equilibrium at these temperatures Also the sample does not go back to its conductivity state that existed just before the first heating cycle.*

Preliminary measurements showed that if the measurements of electrical conductivity of samples are made under air atmosphere there is a spectacular change in electrical conductivity. This showed that the electrical conductivity of these materials is significantly influenced by the ambient atmosphere. We have made detailed investigations of this effect Electrical conductivity measurements were made under the following different atmospheres : (1) air, (2) nitrogen

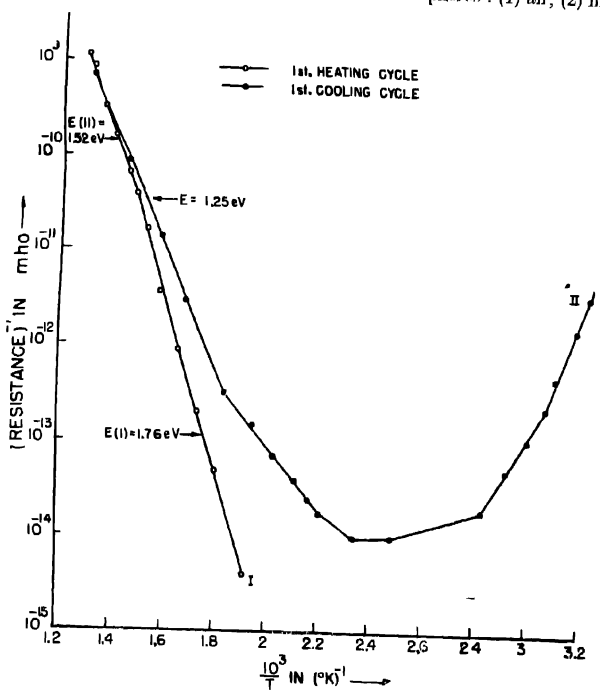

Fig. 2 Two typical log $1/R$ versus $1/T$ curves during heating and cooling cycles for GGG with air ambient atmosphere.

and (3) argon In this paper we shall discuss in detail the results obtained with air as the ambient atmosphere

Figure 2 shows two typical $\log(1/R)$ versus $1/T$ curves with air as ambient atmosphere. Curve 1 is the first heating curve and consists of two straight lines in the temperature regions 523–673°K (region I) and 673–800°K (region II). The values of activation energy, E is found to be 1·76 eV in temperature region I and 1·52 eV in the temperature region II While cooling the sample after first heating cycle, the conductivity plot consists of one straight line This result is similar to that observed in the earlier case (figure 1). The value of activation energy in the cooling cycle is 1·25 eV the same as observed earlier (figure 1). Conductivity is higher during cooling cycle than during heating cycle

An interesting feature of these results is that the presence of air alters the conductivity behaviour of GGG in a very significant manner as compared to its conductivity behaviour under vacuum While cooling under air from 800°K there is a characteristic temperature at which the conductivity of the sample starts increasing with decrease in temperature (curve II in the temperature region 430°K to room tempdcrature). This characteristic temperature is 403°K,

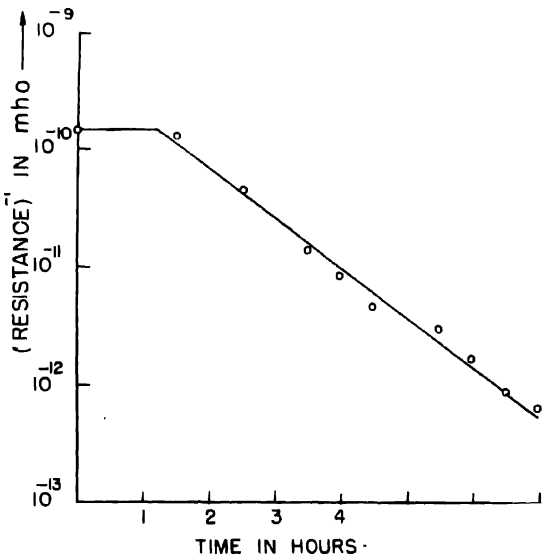

Fig. 3. A typical log $1/R$ versus t (time of exposure to air) curve.

in air as ambient atmosphere. After the first heating cycle the room temperature conductivity of the crystal increases to $10^{-12}\ \Omega^{-1}\ cm^{-1}$, as compared to its conductivity value $10^{-16}\ \Omega^{-1}\ cm^{-1}$, just before this experiment. However, after the sample is removed from the sample holder and exposed, to air it slowly regains its highly insulating state. This process takes about 12 hours of exposure to air. We have studied the change of resistance of the sample as a function of time of exposure to air after it had undergone one heating cycle under air. Figure 3 shows the change in resistance of the sample as a function of time of exposure to air It follows a relation $\sigma \propto e^{-t/T}$ where t is the time of exposure and T is the time constant of the process. The value of time constant is found to be 2 hours 20 minutes as calculated from figure 3.

The electrical conductivity of GGG was also measured with N_2 and Ar as ambient atmosphere. The general variation of electrical conductivity with temperature under these ambient atmospheres is similar to that as observed under air (figure 2).

4. Discussion

Extensive work has been reported on the study of electrical conductivity in doped ferrimagnetic garnets like yttrium iron garnet (YIG) (Elwell & Dixon 1968). In YIG the electrical conduction is considered to take place through hopping of electrons. In this case hopping conduction mechanism is visible due to the possibility of exchange of electrons between Fe^{2+} and Fe^{3+} ions located at equivalent crystallographic sites. In the present case a change of valence in Ga or Gd is not expected. Secondly, GGG has very low conductivity at room temperature which rules out the change of valence of Ga or Gd

The optical absorption spectrum of GGG has shown that it is transparent upto ~ 3200 Å The values of activation energy E in the experimental temperature range suggest that the observed conduction is not due to interband transitions.

Recent work has shown that incorporation of Ar gas atoms give rise to color centres in molybdenum doped YAG (Kvapil *et al* 1975). These color centres arise mainly due to the change of valence of Mo. The change in valence can give rise to conductivity by hopping mechanisms Samples used in the present work were analyzed carefully by spectroscopical method. No significant concentration of impurities like Mn, Fe could be detected. Therefore the hopping mechanism is not likely to be responsible for conduction in these crystals.

The effect of atmosphere shows positively that presence of gas atoms influences the conduction in these crystals. We are not aware of any data on diffusion in these crystals. Therefore it is not possible to give a definite mechanism of conduction in these crystals at this stage. All this data, however, suggests

conduction taking place due to ionic transport in which presence of even inert gases like argon helps. The charge carriers are normally in aggregates at room temperature and they dissociate only on heating at 678°K and above. The aggregation obeys a simple monomolecular law with a fairly long time constant.

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