MATERIALS FORUM VOLUME 29 - Published 2005
Edited by J.F. Nie and M. Barnett
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ELECTRICAL AND OPTICAL PROPERTIES OF $ZnGa_2O_4$ THIN FILMS DEPOSITED BY PULSED LASER DEPOSITION

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ABSTRACT

$ZnGa_2O_4$ spinel is a promising new UV transparent electronic conductor. Enhancing the electrical conductivity of this potential oxide phosphor can make it a promising transparent conducting oxide. In this paper, we have investigated the effects of processing and doping on the conductivity of semiconducting $ZnGa_2O_4$, particularly thin films. Crystalline zinc gallate thin films have been deposited on fused quartz substrates employing the pulsed laser deposition (PLD) technique at room temperature for an oxygen partial pressure of 0.1 Pa (0.001mbar)**.** The films were found to be UV transparent, the band gap of which shifted to 4.75eV on hydrogen annealing. The band gap of the oxygen stoichiometric bulk powder samples (4.55eV) determined from diffuse reflection spectrum (DRS) shifted to 4.81eV on reduction in a hydrogen atmosphere. The electrical conductivity improved when Sn was incorporated into the $ZnGa_2O_4$ spinel. The conductivity of $ZnGa_2O_4$:Sn thin films was further improved on reduction.

1. INTRODUCTION

One of the important fields of current interest in material science is the fundamental aspects and applications of semiconducting transparent thin films. In most conductive or semiconductive materials, strong absorption in the visible region precludes the simultaneous occurrence of both good conductivity and good transparency. The charge buildup at the phosphor surface due to its high resistivity is the drawback of low voltage field emission display (FED) applications [1]. Therefore, new materials with good transparency and improved conductivity would be of interest to the rapidly developing technology of flat panel optical displays [2-5]. Moreover, transparent conducting oxides (TCO) are essential part of technologies that require large area electrical contact and optical access in the visible portion of the electromagnetic spectrum.

Optical transparency and metallic conductivity are the properties of solids almost antonymous to each other. A few solids exhibiting both these properties simultaneously, indium tin oxide (ITO) and the doped ZnO and SnO_2, are excellent TCOs [6]. Because of this unique nature, these materials have been widely used as a transparent electrode in liquid crystal displays (LCD) and solar cells. Higher transparency and /or higher conductivity than those of the materials commercially available are requested in the development of the photoelectronic devices such as large area colored LCDs, FEDs, etc**.** The possible materials are almost limited to oxides, fluorides and some chlorides. It was assumed that oxides with the spinel structure, in which at least one of the cations involved has $d^{10}s^0$ electronic configuration, are very promising as new transparent conductive materials. Oxide thin-film phosphors also have received considerable attention for use in flat-panel displays due to their good luminescent characteristics, stability in high vacuum, and absence of corrosive gas emission under electron bombardment when compared to currently used sulphide-based phosphors. Other semiconducting spinel oxides investigated for their electroconductive properties include $MgIn_2O_4$ (E_g=3.4eV) [7] and $CdGa_2O_4$ (E_g=3.1 eV) [8]. Of these spinel structures, semiconducting $ZnGa_2O_4$ is unique in providing transparency into the ultraviolet region.

$ZnGa_2O_4$ is an interesting double oxide with the spinel crystal structure and is composed of only the fourth row cations. It is an attractive phosphor host candidate material for flat panel displays because of its favorable photoluminescent (PL) and cathodoluminescent (CL) properties and excellent mechanical and thermal stability. With a wide band gap of 4.4-5eV, semiconducting $ZnGa_2O_4$ is potentially useful as a transparent conducting oxide, particularly if transparency through the violet to near UV spectrum is desired. The inherent problem of $ZnGa_2O_4$ for phosphor applications is its poor electrical conductivity, which accumulates electrons on the phosphor screen and leads to the degradation of the luminance efficiency [9]. Moderate conductivity can be introduced by annealing in a reducing atmosphere at high temperatures. The poor electrical conductivity of $ZnGa_2O_4$ can also be remedied by doping. The doping of SnO_2 in $ZnGa_2O_4$ phosphor is found to enhance the electrical conductivity of $ZnGa_2O_4$ through the solid solution formation of $ZnGa_{2-x}Sn_xO_4$ phosphors [10].

Several methods have been used to synthesize polycrystalline $ZnGa_2O_4$ thin film phosphors, including sputtering [11,12], sol-gel processing [13], chemical vapor deposition [14] and PLD [15,16,17,18]. Thin film phosphors have several advantages in comparison to the powders, such as higher lateral resolution from smaller grains, better thermal stability, reduced outgassing, and better adhesion to the solid surface [19]. However, the biggest drawback in the use of phosphor thin films is their low brightness and efficiencies in comparison to those of bulk powder materials which are primarily associated with factors such as internal reflection, the small interaction volume between incident beam and solid and absorption of generated light by substrate materials.

The deposition of crystalline $ZnGa_2O_4$ phosphor thin films by PLD on amorphous glass substrate at room temperature has been reported [20]. The PLD address two criteria better than other methods namely precise relative arrival rates of atoms for compound films and the ability to operate in high pressure reactive gases. The as deposited films exhibit poor crystallinity and inferior luminescent properties; improvement of which requires post deposition annealing at high temperature ~1000^0C [15].

This paper elucidates the effects of processing and doping on the conductivity of semiconducting $ZnGa_2O_4$, particularly thin films.

2. EXPERIMENTAL PROCEDURES

2.1 Synthesis of bulk samples of $ZnGa_2O_4$ and $ZnGa_2O_4$:Sn

Pure $ZnGa_2O_4$ powder was prepared by mixing ZnO and Ga_2O_3 in the 1:1 ratio in ethyl alcohol medium and then calcined at 1000^oC for 12hrs. Similarly, the $ZnGa_2O_4$:Sn powder was prepared by mixing ZnO, Ga_2O_3 and SnO_2 stoichiometrically in ethyl alcohol medium and then calcined at 1000^oC for 12hrs. The concentration of Sn was fixed at 5 atomic%. The calcined powders were then pressed into a disk of ~1cm diameter and then sintered at 1200^o C for 12hrs in air. The samples were annealed in a reducing atmosphere (hydrogen) at 700^oC for 5hrs to generate oxygen vacancies. The bandgap of pure $ZnGa_2O_4$ powder was determined by recording the diffuse reflectance spectrum (DRS) at room temperature with MgO as reference using Ocean Optics, Inc. SD 2000, fiber optic spectrometer with a CCD detector. The electrical conductivity of the pure and annealed samples was measured using a Keithley 236 Source Measure Unit.

2.2 Deposition of thin film samples of $ZnGa_2O_4$ and $ZnGa_2O_4$:Sn

The $ZnGa_2O_4$ target, for laser ablation, was synthesized in the laboratory by solid state reaction. The $ZnGa_2O_4$ powder is pressed into a disk with 25mm diameter and 8mm thickness and then sintered at 1350^oC for 36hrs in air.

The films were grown by PLD using a Q-switched frequency doubled (532nm) Nd:YAG laser. The beam of Nd:YAG laser was focused on to the surface of the target with a spot size of 2mm diameter. The distance between the substrate and the target was kept at 9cm. The laser power was 0.2watts, repetition frequency 10Hz and pulse duration 9 ns. The target was rotated continuously during deposition at 23 rpm. Fused quartz was used as the substrate. The deposition was carried out at room temperature (30^oC) at an oxygen partial pressure of 0.1 Pa (0.001mbar). The samples were then annealed in a reducing atmosphere (hydrogen) at 700^oC for 5hrs to generate oxygen vacancies. The structural characterization of the films was done using an X-ray diffractometer (Rigaku) using Cu-Kα radiation (1.5414 Å). The transmission spectra of the thin films were recorded using a UV-VIS-NIR spectrophotometer (Hitachi U 3410). The electrical conductivity of the pure and annealed samples were measured using a Keithley 236 Source Measure Unit. The PL spectra were measured at room temperature with an excitation wavelength 260nm using a 450W xenon lamp.

3. RESULTS AND DISCUSSION

The X-ray diffraction pattern (Fig.1) of the as deposited and hydrogen annealed films have a peak which can be indexed to $ZnGa_2O_4$ (111). Crystalline films were grown on quartz substrates at room temperature. The presence of an unidentified peak in the X-ray diffraction pattern of the thin film indicates the presence of impurity phases.

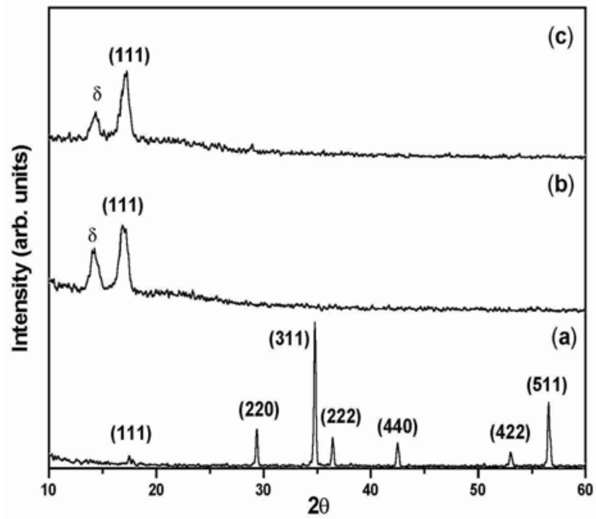

Figure 1: X-ray diffraction patterns of a) $ZnGa_2O_4$ target, b) as-deposited $ZnGa_2O_4$ thin film and c) hydrogen annealed $ZnGa_2O_4$ thin film; δ- unidentified peak

Similarly, the X-ray diffraction pattern (Figure 2) of the as deposited and hydrogen annealed films of $ZnGa_2O_4$:Sn also possess the peak which can be indexed to $ZnGa_2O_4$ (111). Crystallinity is observed for the films deposited at room temperature. The low intensity X-ray diffraction peaks, which cannot be indexed to $ZnGa_2O_4$ or constituent oxides, were present in the thin films as well as in the target. The crystallinity was improved on annealing the $ZnGa_2O_4$ film in hydrogen atmosphere, which is indicated by the increase in the intensity of (111) orientation. The shift in the (111) peak can be attributed to oxygen deficiency in the PLD films, which is evident from the blue shift in the PL spectrum. The oxygen deficiency causes a lattice expansion due to the cation-cation repulsion.

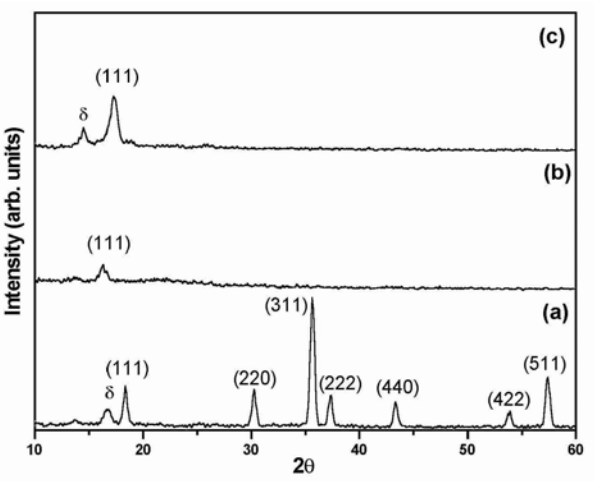

Figure 2: X-ray diffraction patterns of a) $ZnGa_2O_4$:Sn target, b) as-deposited $ZnGa_2O_4$:Sn thin film and c) hydrogen annealed $ZnGa_2O_4$:Sn thin film; δ- unidentified peak

The diffuse reflectance spectra of powder samples of as-prepared $ZnGa_2O_4$ and reduced $ZnGa_2O_4$, ZnO and Ga_2O_3 are given in figure 3. The samples for DRS are generally prepared as a mixture in a non-absorbing and effectively scattering medium such as MgO. The absolute reflectance at infinite depth in the Kubelka - Munk function is then replaced by reflectance of the sample relative to the non-absorbing medium**.** The optical absorption edge of hydrogen annealed $ZnGa_2O_4$ appears almost at 260nm, which is smaller than pure $ZnGa_2O_4$ and reduced ZnO and Ga_2O_3. This indicates that the reduced $ZnGa_2O_4$ spinels have a larger band gap. The reflectance of the H_2 annealed $ZnGa_2O_4$

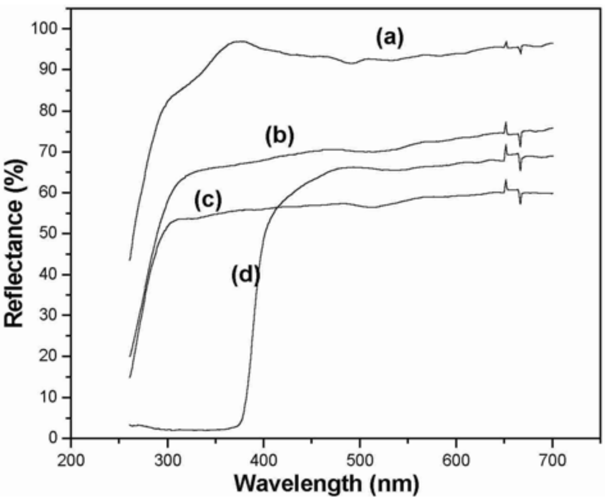

Figure 3: Diffuse reflectance spectrum of (a) H_2 annealed $ZnGa_2O_4$ (b) pure $ZnGa_2O_4$ (c) H_2 annealed Ga_2O_3 (d) H_2 annealed ZnO.

sample is higher when compared with the pure $ZnGa_2O_4$ as well as the reduced ZnO and Ga_2O_3. This indicates the greater carrier concentration of H_2 annealed $ZnGa_2O_4$ [21]. The band gap of the pure and annealed $ZnGa_2O_4$ samples are estimated from a plot of $\{(k/s)h\nu\}^2$ vs hν (Fig 4) where k and s denotes the absorption and scattering coefficients respectively and hν is the photon energy. The ratio (k/s) was calculated from the reflectance via the Kubelka-Munk equation [22,23].

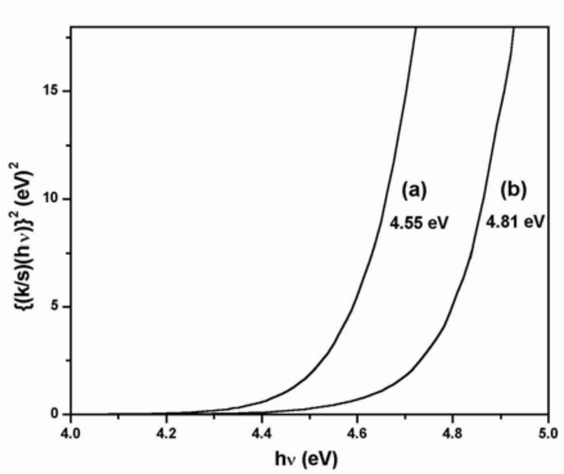

Figure 4: Plot of $\{(k/s)h\nu\}^2$ vs energy of a) Pure $ZnGa_2O_4$ b) reduced $ZnGa_2O_4$.

The band gap of H_2 annealed $ZnGa_2O_4$ is found to be 4.81eV that is larger than ITO (3.7eV) and is different from ZnO in spite of the presence of Zn^{2+} cation [21]. The increase in bandgap may be due to an increase in carrier concentration, as a result of which the absorption edge shifts towards the near UV range. The increase in bandgap energy with carrier concentration can be explained on the basis of Burstein-Moss (B-M) effect. Assuming that the conduction band and valence band are parabolic in nature and that B-M shift is the predominant effect, we can write

$$E_g=E_{g0}+\Delta E_g^{B\text{-}M}$$

where E_{g0} is the intrinsic bandgap and $\Delta E_g^{B\text{-}M}$ is the BM shift due to filling of low lying levels in the conduction band [24]. An expression for B-M shift is given by

$$\Delta E_g^{B\text{-}M} = (h^2/8\pi^2 m_{vc}^*)(3\pi^2 n)^{2/3}$$

where n is the carrier concentration and m_{vc}* is the reduced effective mass of the carriers. From this expression it is clear that B-M shift is directly proportional to carrier concentration.

The bandgap of the $ZnGa_2O_4$ films were also determined from the transmission spectra (Figure 5). By assuming a parabolic band structure for the material, the absorption coefficient and bandgap can be related by the expression

$$\alpha h\nu = A\,(h\nu - E_g)^{1/N} \quad (N=2)$$

where E_g is the band gap energy and α is the absorption coefficient corresponding to frequency ν [25]. The bandgap of thin films were determined from the plot of $(\alpha h\nu)^2$ vs hν (inset of figure 5). By extrapolating the linear portion of the curve to hν equal to zero, it is found to be 4.54eV. The film post-annealed in a reducing atmosphere shows a wider band gap of 4.75eV. This increase in bandgap energy with carrier concentration can be explained on the basis of Burstein-Moss effect as for bulk samples.

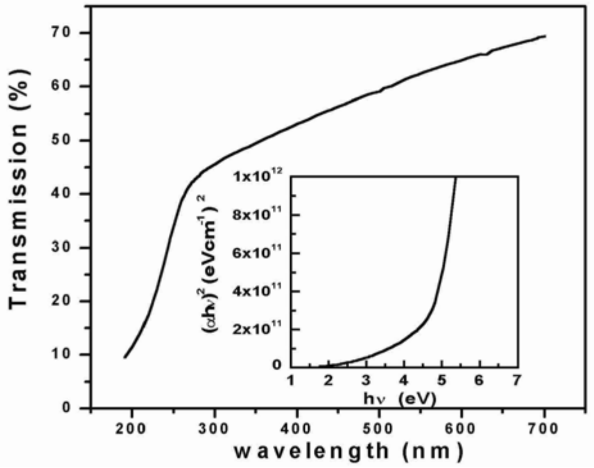

Figure 5: Transmission spectra of $ZnGa_2O_4$ film deposited at 0.1 Pa (0.001mbar) pressure. Inset shows the plot of $(\alpha h\nu)^2$ vs energy

The PL emission spectra of bulk $ZnGa_2O_4$ phosphor and thin film samples (Fig 6) are compared. The emission spectra were recorded under an excitation $\lambda_{ex} = 260$nm. The PL emission characteristics of $ZnGa_2O_4$ films grown by PLD at room temperature are similar in comparison with films prepared at higher substrate temperature (18).

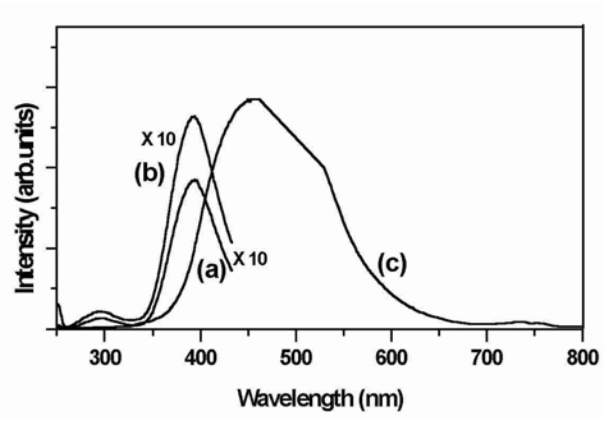

Figure 6: PL emission spectra of a) as deposited $ZnGa_2O_4$ film, b) film annealed at 500°C in air and c) bulk powder sample

The emission spectrum of $ZnGa_2O_4$ showed a broadband peaking at 437nm that can be attributed to the self activated centers originating from the octahedral Ga-O group in the normal spinel lattice of $ZnGa_2O_4$ [26]. The Commission International d'Eclairage (CIE) coordinates of the pure sample is found to be x = 0.184, y = 0.322 which supports the blue emission. Room temperature PL emission spectra of $ZnGa_2O_4$ thin films grown by PLD shows a broad band with a peak at 394.4nm.

The blue shift of PL emission of the $ZnGa_2O_4$ film compared to bulk $ZnGa_2O_4$ suggests that the PLD films are oxygen deficient. The oxygen vacancies are most probably associated with the formation of Ga^+ ions. The blue emission has been speculated to be related to the formation of new self activated optical centers due to the tetrahedral Ga-O groups in the spinel lattice [27,28]. The CIE coordinates is found to be x = 0.17 and y = 0.005 for the as deposited film. The film annealed at 500°C shows a similar spectrum. But the luminescence is significantly greater. This can be attributed to the improved crystallinity during annealing.

To enhance the conductivity of $ZnGa_2O_4$, it is doped with 5 atomic% of Sn to form $ZnGa_{1.95}Sn_{.05}O_4$. The temperature dependence of the electrical conductivity of bulk and thin film samples (Figure 7 and Figure 8) were measured in the temperature range 70K to 300K. The variation of conductivity is plotted as a function of reciprocal temperature (1000/T). The hydrogen annealed $ZnGa_2O_4$ powder samples show an increase in conductivity with temperature typical of a semiconductor. The tin substituted samples, after hydrogen annealing, shows an improvement in conductivity by one order compared to the undoped hydrogen annealed $ZnGa_2O_4$ powder.

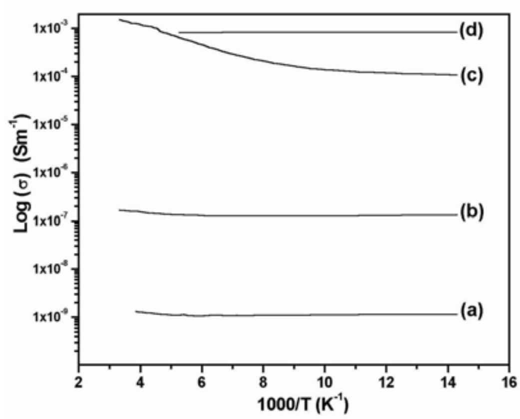

Figure 7: Conductivity of bulk a) $ZnGa_2O_4$ b) $ZnGa_2O_4$:Sn c) hydrogen annealed $ZnGa_2O_4$ d) hydrogen annealed $ZnGa_2O_4$:Sn

The conductivity of the H_2 annealed samples is higher than that of the pure samples without any intentional doping. It can be inferred that the formation of conduction electrons was enhanced under reducing conditions. This also suggests that oxygen vacancies, created while reduction, acts as the orgin of the source of conduction electrons. The electrons are thermally excited from oxygen vacancies to the conduction band to which Zn 4s and Ga 4s orbitals mainly contribute. The non-Arrhenius like behavior of H_2 annealed $ZnGa_2O_4$ samples originates from the degeneration of electrons created by oxygen vacancies [8]. Doping with Sn is found to enhance conductivity.

The conductivity of the thin film samples are rather low. This may be due to the poor crystallinity and also due to the fact that the Zn to Ga ratio may deviate from the stoichiometric value due to the higher vapor pressure of Zn. Moreover, all the tin atoms substituted

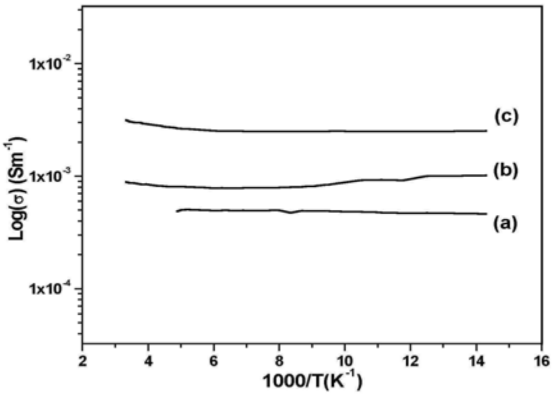

Figure 8: Conductivity of a) pure $ZnGa_2O_4$ film b) Hydrogen annealed $ZnGa_2O_4$ film c) Hydrogen annealed $ZnGa_2O_4$:Sn film

for gallium in the bulk may not be incorporated in the film. Further optimization of the deposition condition and the doping concentration can improve the stoichiometry and conductivity of the film.

4. CONCLUSIONS

The diffuse reflectance spectrum of $ZnGa_2O_4$ spinel indicates that its optical band gap (4.5eV) is much larger than that of ITO (3.7eV). The H_2 annealed $ZnGa_2O_4$ spinel has a wider band gap (4.8eV) than the pure sample. Crystalline $ZnGa_2O_4$ thin films were grown on amorphous glass substrates at room temperature by PLD technique. $ZnGa_2O_4$ spinel is therefore a promising material as a UV- transparent electronic conductor. The H_2 annealed $ZnGa_2O_4$ powder shows an increase in conductivity than pure $ZnGa_2O_4$ without any intentional doping. Substitution of Sn in the $ZnGa_2O_4$ spinel structure improves the conductivity.

ACKNOWLEDGEMENT

This work is supported by Department of Science and Technology and University Grants Commission, Government of India. The authors MKK and NM wish to thank the CSIR for the Research Fellowship and MKJ thanks the Kerala State Council for Science, Technology and Environment, Government of Kerala for the financial support under SARD programme.

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