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STRUCTURAL, VIBRATIONAL AND OPTICAL PROPERTIES OF EU^{2+}AND DY^{3+} DOPED $SRAL_2O_4$

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ABSTRACT

Polycrystalline $Sr_{0.96}Eu_{0.02}Dy_{0.02}AlO_4$nano-material has been successfully prepared by combustion method. The sample was found to have crystallized in monoclinic structure of single phase nature with the assigned space group of $P2_1$. The crystallite size was found to be ≈ 13 nm. Further confirmation of structure was done by Raman spectroscopy. The modes about 400cm^{-1} confirmed extremely small crystallite size and merging of other modes in the vicinity of the main mode. Due to double-doping, the possible peaks due to monoclinic phase have been found to disappear that can be revisioned in low temperature Raman. The UV-Vis spectrum analysis confirmed the extreme narrowing of bandgap compared that of the parent $SrAl_2O_4$which is about 4eV.

Keywords- *1. Aluminates, 2. XRD, 3. Raman spectroscopy, 4. Optical properties*

I. INTRODUCTION

Phosphor is a material which converts certain type of incident energy into electromagnetic energy. The incident energy may be ultraviolet, ϒ radiation etc., which serves as the excitation source **[1].** Certain nano powders are depending on the point defects hence small amount of dopant brings drastic change in colour emission. Alkaline earth aluminates MAl_2O_4 (M = Ca, Sr, and Ba) are themost widely used potential phosphormaterials for use in photonics applications, such as display technology and lighting. Among all other phosphors, strontium based aluminate phosphors are well known for their high quantum efficiency, long-lived afterglow, good chemical stability and other excellent luminescent features, which make them appropriate candidates to replace the traditional II–VI based phosphors. These materials are successfully used in various applications from luminous paints for highways, airport, buildings, ceramic products, textile industry, the dial plate of glow watches, to warning signs and escape routes, etc. **[2,3].**

$SrAl_2O_4$ has attracted much interest of the researchers in recent years owing to its excellentluminescent properties such as long duration and highbrightness. In addition, $SrAl_2O_4$ material is chemically morestable than sulphide phosphors. The $SrAl_2O_4$ based phosphor materials are prepared via sol-gel, solid state reaction,co-precipitation and others. Among of all othertechniques, combustion synthesis method is very simple, safe, energy saving and takes only a few minutes to prepare theoxide materials. This method is based onredox reaction, in which heat is liberated atlow igniting temperaturebetween metal nitrates and urea as fuel. The heat energy so produced is used for thepreparation of the phosphor**[4,5].** It was found that the $SrAl_2O_4$:Eu^{2+} prepared at initiating temperature 600^oCexists as a single phase monoclinic structure **[6].**

Many reports available on $SrAl_2O_4$: Eu^{2+}, Dy^{3+} and other rare earths can be used for cold lighting purposes. This is explained on the basis of trapping mechanism between ground state and excited state. Now a day's one dimensional inorganic nano structures attracts people because of their high end applications in electronics and optics. Since the aluminate phosphors are very sensitive to humidity hence many research going on the strontium aluminate to improve water resistant properties. The photo luminescence properties depend on phase of the material **[7,8].**

In the present stud our focus will be the structural, vibrational and optical properties of the $SrAl_2O_4$: Eu^{2+}, Dy^{3+} nano-material. Since these materials are studied much as per their luminescence effect but hardly there is any report

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on the study of band gap and hence bandgap related properties like emission and electrical properties like dielectric properties of these materials. So we have taken initiative to study these aluminate materials some different way and present study is the step in the new way study of these materials.

II. EXPERIMENTAL DETAILS

The $SrAl_2O_4$: Eu^{2+}, Dy^{3+} samplewas prepared by easy, conventional and energy saving chemical combustionprocess. The starting materials were $Sr(NO_3)_2$, Al_2O_3, Eu_2O_3 and Dy_2O_3 analytic grade of purity of the order of 99 plus from High Medial Chemical company. Initially the stoichiometric amounts were taken where $Sr(NO_3)_2$ and Al_2O_3 were added in separate tube. The rare earth oxides were taken inother tube inwhich few drops of concentrated HNO_3 was added to convert them into nitrates. Then the materials in two tubes were taken into Motor-pestle where urea is added as fuel and 20% of the whole material boric acid will be added. The components are mixed thoroughly until a paste is formed. The paste is then taken into crucible and put on furnace at 600 ^oC. The sample catches fire at low ignition temperature and an ash of white colour is formed which is then ground for an hour and is ready for characterization**[8].**

The crystal structure and type of phase of the sample was identified by means of X-ray powder diffraction technique at room temperature, using Bruker D8-Advance X-ray diffractometer with $CuK\alpha_1$ (1.5406 Å) radiation. The data was collected with a step size of 0.02° over the angular range 2θ (10°< 2θ< 80°) generating X-ray by 40 kV and 40 mA power settings. The Raman measurement was carried out using LABRAM - HR800 spectrometer equipped with a 50 × objective, and a Peltier-cooled charge coupled device detector. The sample was subjected to radiation of 488 nm as exciting source (2.53 eV) from an air-cooled Argon Laser. UV-Vis spectrometer (Perkin Elmer, Lambda 950 - USA) was used to find the band gap of all the samples under investigation

III. RESULTS AND DISCUSSIONS

The structural characterization of obtained sample was performed by XRD analysis. The XRD pattern of as-synthesized product is shown inFigure.

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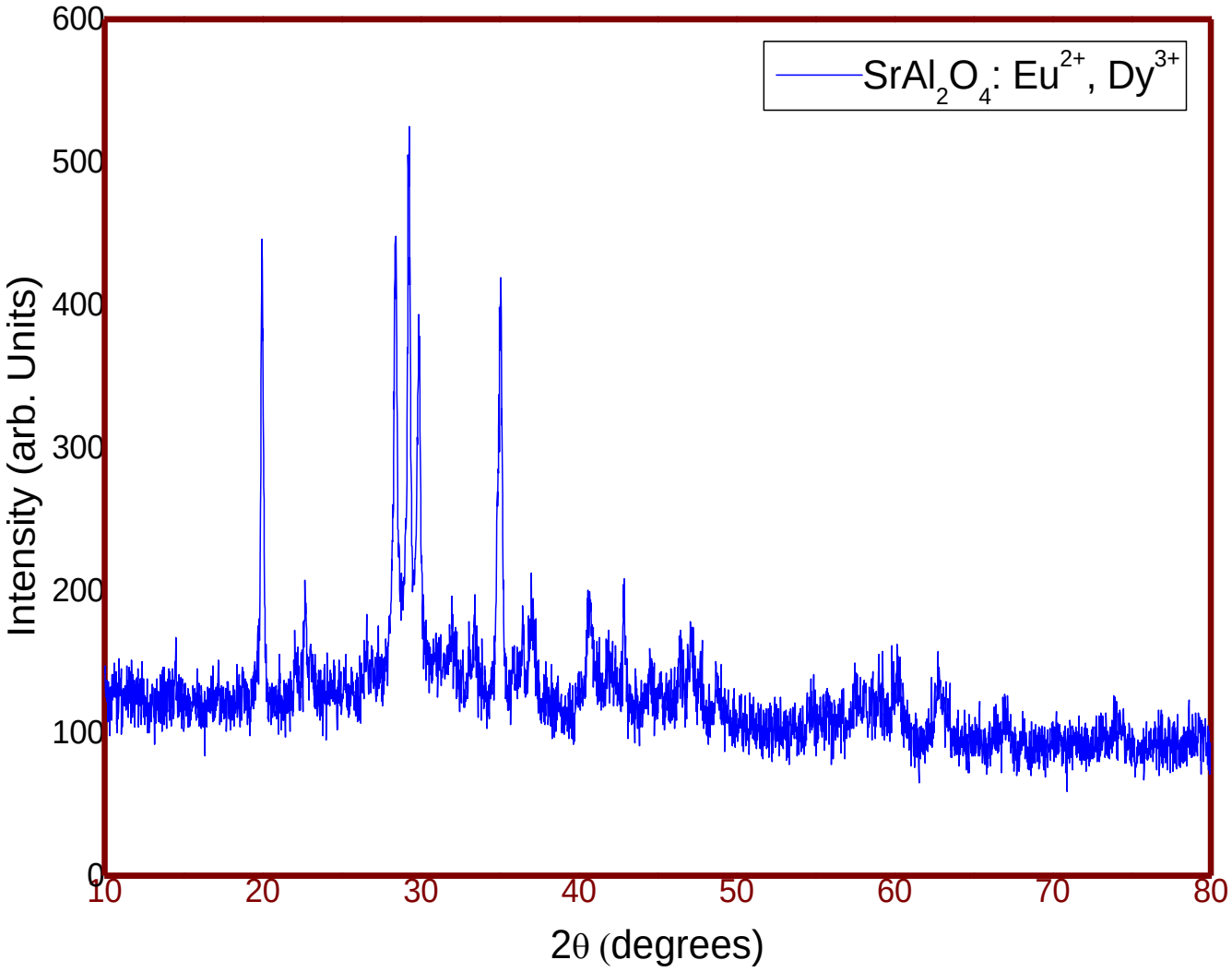

Figure 1: XRD spectrum of the synthesized $SrAl_2O_4$:Eu^{2+}, Dy^{3+}nanocrystallinesample.

The $SrAl_2O_4$: Eu^{2+}, Dy^{3+} sample was found to crystallize in monoclinic structure (space group $P2_1$). The unit cell parameters are calculated to be *a* = 8.4329 Å, b=8.8196and *c* = 5.0982 Å with β= 94.012°.

The broadness of characteristic diffraction peaks and low intensity but sharpness indicate the low particle size, crystalline with associated porosity in the sample.

The average crystallite size of ferrites powder has been calculated using Debye–Scherer formula [9]:

$$D = 0.9\lambda / \beta \cos\theta$$

Here, λ is the wavelength of the Cukα1 radiation (λ = 1.54060 Å), and β is the full width at half maximum, k is shape factor (k = 0.9) and the calculated particle size was found to be 13nm.The lattice parameters of the specimen, evaluated by XRD analysis are given above and slight variation from the report is attributed to the thermal effects

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and light variation in the ionic radii of the dopants compared to the ionic size of the Sr ion. The results are in agreement with the report **[10].**

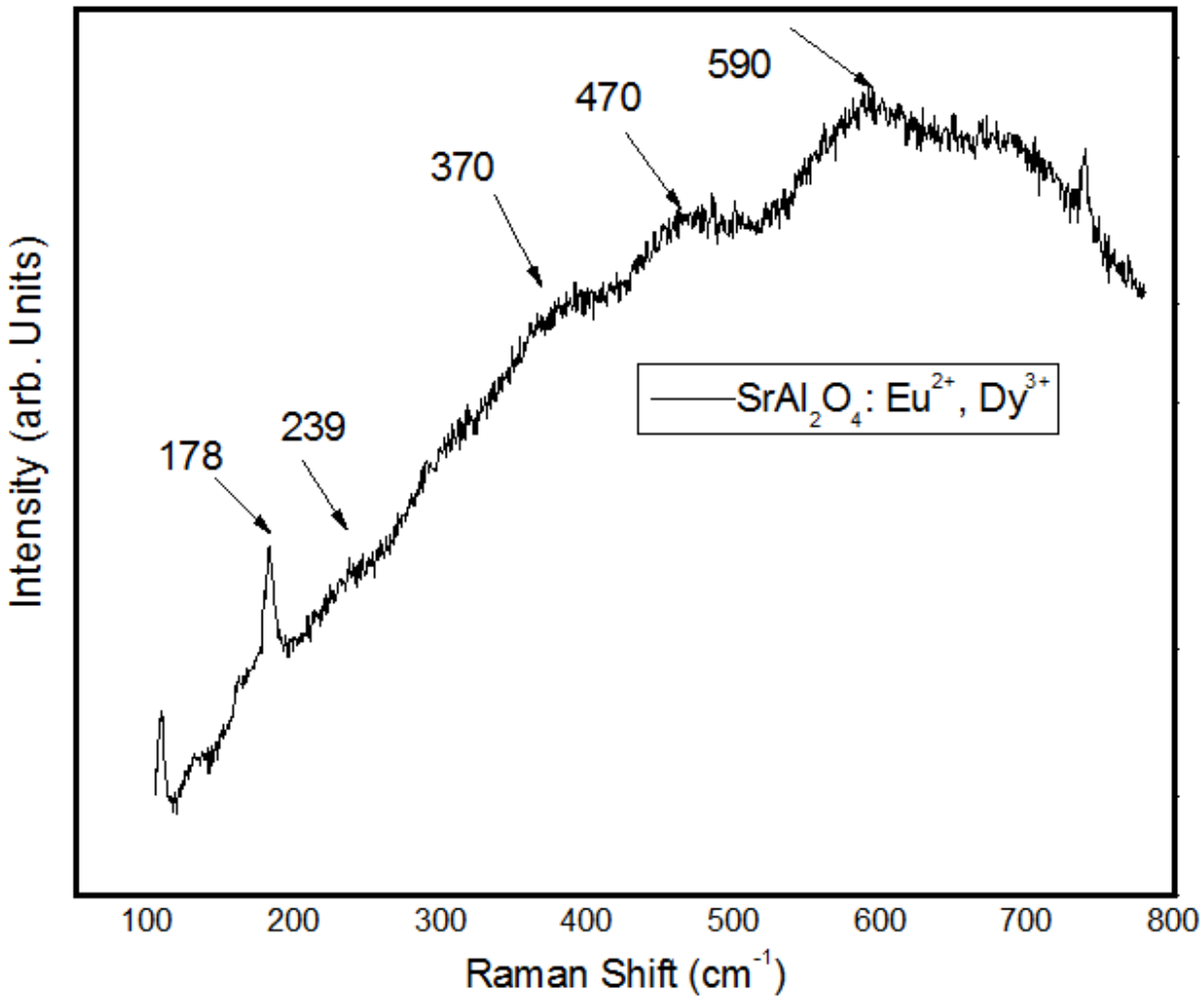

Figure 2: Raman Spectrum of the $SrAl_2O_4$:Eu^{2+}, Dy^{3+} material.

displaysthe Raman spectrum of the $SrAl_2O_4$: Eu^{2+}, Dy^{3+}nanocrystalline samples. Raman spectroscopy is very sensitive to the structure and bond order of metal oxides, especially in the region of metal–oxygen stretching modes, because many of the Raman frequencies depend on the bond order in the structure. A higher metal–oxygen bond order, corresponding to a shorter bond distance, shifts the Raman bond to higher wave numbers. Raman spectrum of the prepared sample was obtained at room temperature in the range 100- 800cm^{-1}.The spectrum so obtained shows several differences from that of reported but on thing is clear that respective peaks are at their original position with slight shift. The reported strongest phonon mode above 500 cm^{-1} has extremely weakened with increased width which is indication that Eu and Dy doping has resulted in the considerable lattice distortion **[11].**

The intermediate mode of vibration at 470cm^{-1} is attributed to the bending of O–Al–O bonds in corner-sharing tetrahedral, indicating that the polymorph as present very closely structure. To interpret Raman spectrum, the lack of polarization measurements and the expected mixing of atomic shifts prevent mode assignment. As structures built up of linked tetrahedral units, it is usual to discuss the Raman spectrum interms of internal vibrations of the MO4 unit. To a first approximation, we attribute modes at frequency higher than 600cm^{-1} to Al–O bond-stretching

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vibrations and the narrow, low-frequencypeaksbelow250cm^{-1}as shown to tetrahedral vibrations or tilts. Higher Raman shifts are probably due to multiphonon or electronic Raman processes**[12].**

The optical band gapwas estimated by plotting Kubelka-Munk function $[F(R)h\nu]^{1/2}$ against energy represented by

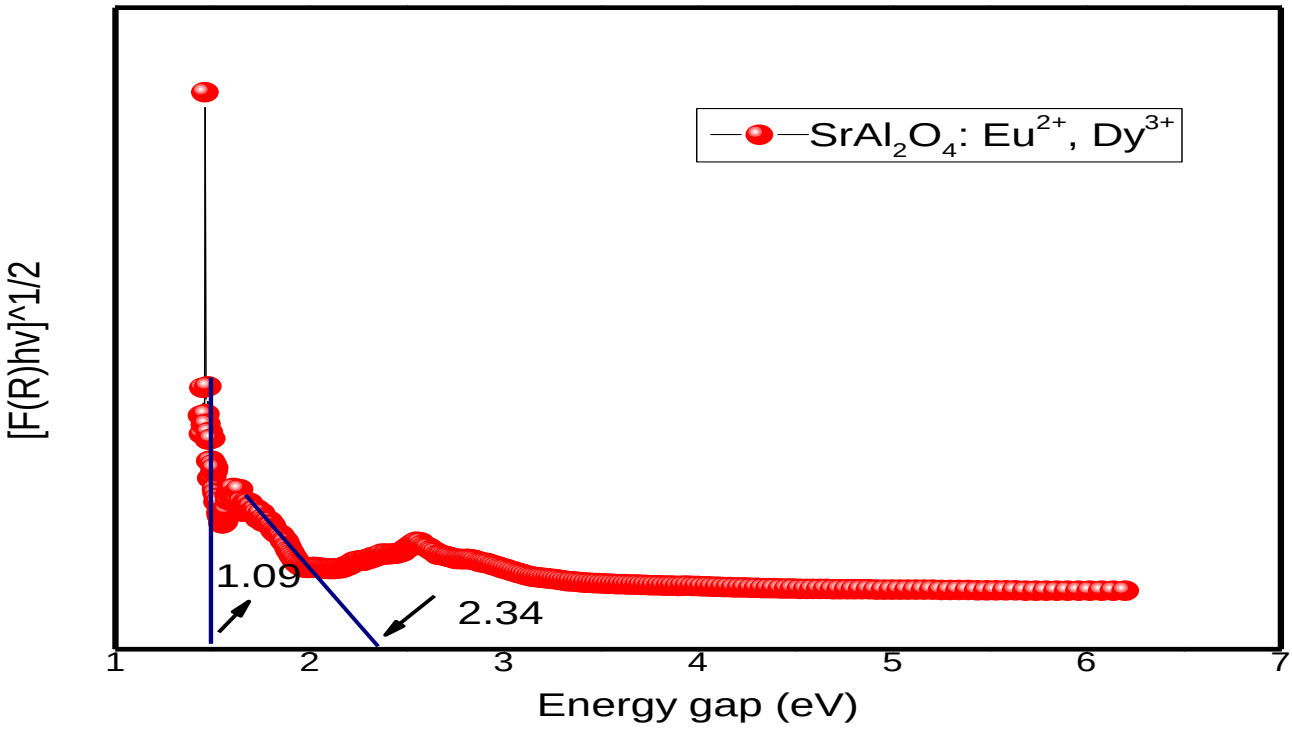

Figure 3: UV-Vis Characterization of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} sample

The $SrAl_2O_4$: Eu, Dy sample was found to have two band gaps of the order of 1.09and 2.34 eV. The narrowing of band gap of the prepared sample compared to reported bandgap of pure $SrAl_2O_4$ which is ≈4 eV is backed by theoretical explanations based on sed and ped exchange interactions employing the second-order perturbation theory **[13].**

IV. CONCLUSIONS

In summary, we have synthesized $SrAl_2O_4$:Eu^{2+}, Dy^{3+}nanocrystalline sample using chemical combustion method.X-ray diffraction (XRD) confirmed the single-phase monoclinic structure (space group $P2_1$). for the prepared sample. The Raman Spectrum confirmed strongest phonon mode above 500 cm^{-1} has extremely weakened with increased width which is indication that Eu and Dy doping has resulted in the considerable lattice distortion. Also UV-Vis characterization has confirmed two band gaps for the prepared sample.

V. ACKNOWLEDGEMENT

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