A Review on Study of Synthesis, Luminescence Properties and Heating Effect on Cation Doped Garnet Structure

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Abstract

In this review, first we discuss detailed study of garnet structure with various dopant like Tb^{3+}, Tb^{2+}, Y^{3+}, Ce^{2+}, Ce^{3+}, Eu^{3+}, Eu^{2+}, Al^{3+} and Tm^{3+} etc. The choice of synthesis method depends on the specific requirements of the application and the desired properties of the garnet-structured nanoparticle phosphors. Researchers often fine-tune the synthesis parameters to achieve the desired particle size, morphology, and luminescent properties. Additionally, post-synthesis treatments, such as annealing or surface modifications, may be employed to further enhance the phosphor's performance. It is observed that the structure of the garnets crystal is cubic and belongs to cubic phase and (Ia3d) space group. The researchers were worked with the garnet components as host and activated by lanthanide trivalent dopants in the range of nanoscale materials. The product materials were used for white LED after investigation of excitation and emission wavelength at different temperature with different heating time.

Keywords: A. Garnet Structure; B. Phosphors; C. Luminescence; D. Heating effect; E. Lanthanide trivalent dopant.

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Introduction

Nanoscience and nanotechnology have become very popular technology since last 30 years [1]. Luminescence is the emission of light observed when a material absorbs energy and re-emits it in the form of visible or invisible light. Luminescent phosphor nanoparticles with a garnet structure have gained significant attention for their use in various applications, including high-efficiency LED lighting, displays, optics, spanning from lighting to lasers, solar energy, optical imaging and bioimaging [2]. Garnet-structured phosphors are typically composed of rare earth ions (dopants) in a host lattice of garnet structure. The most common host lattice for garnet phosphors is yttrium aluminium garnet (YAG). The crystal structure of the host lattice influences the luminescent properties. Rare earth ions (e.g., cerium, europium, and terbium) are introduced as dopants into the garnet structure. These dopants play a crucial role in the luminescence process. They are responsible for absorbing energy and emitting light of different colors.

The luminescent mechanisms in garnet phosphors involve energy absorption through various processes like absorption of UV or blue light, and subsequent emission in the form of visible light (e.g., green or red luminescence). The luminescence efficiency and temperature dependence of garnet phosphors are essential considerations. Some phosphors may exhibit reduced luminescence at higher temperatures, which is an important factor to account for in practical applications. The stability and lifetime of the luminescence are important for the long-term performance of devices that use garnet phosphors [3]. The choice of dopants and the synthesis process can impact these factors. The synthesis of garnet phosphors is a critical aspect of their luminescence characterization. Various methods, including solid-state synthesis and sol-gel processes, are employed to create these materials with precise control over their properties. The luminescent properties of garnet-structured phosphors are closely related to their composition, crystal structure, and synthesis methods. Researchers in materials science and solid-state physics continue to study and develop new garnet phosphors with enhanced luminescent characteristics for various technological applications.

In last decade, various researchers have published many review articles on garnet phosphors. For this reason, we would have liked to concentrate here on a specific class of oxides category nanocrystalline materials doped with Ln3+. In this review, we have to more focus on bulk and nanoparticle garnet materials. The synthesis of garnet-structured nanoparticle phosphors typically involves various methods, each with its own advantages and disadvantages [4]. The choice of synthesis method depends on factors like desired particle size, purity, and the specific rare earth dopants required.

Finally, discuss the particle size effects on their chemical and optical spectroscopic properties. Characterization should also include studying the stability of luminescence and its temperature dependence. Some nanoparticles may exhibit thermal quenching, where their luminescence decreases at higher temperatures

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The Garnet Family

The general chemical formula of the family of garnet crystals can be expressed as $A_3B_2C_3O_{12}$; where B and C can be the same (i.e. $Y_3Al_2Al_3O_{12}$) or different atoms (i.e. $Ca_3Sc_2Si_3O_{12}$). The structure of the garnets crystal is cubic and belongs to cubic phase and (Ia_3d) space group. Some other crystalline materials have the formula $A_3B_2C_3O_{12}$ (i.e. $Ca_3Y_2Si_3O_{12}$) but has different crystal structural properties, due to detrimentally superposition of the radii of the ions addressed in the sites A and B [5-6]. The garnet structural materials possesses three crystallographically different positions (c, a, and d) at where the whole site symmetry groups are conjugated known as Wyckoff positions which are available for arrangement of dopant/guest ions. The D2 symmetry denoted by the c position, here S6 symmetry denoted by the ‘a’ position and the S4 symmetry denoted by the d position. An oxygen tetrahedron surround about C ions.

The native defects appear in the garnet structure is depending on heating time and temperature during crystal growth also depends on methodology. The intrinsic, anti-site defects (which is commonly found in semiconductor) are dominant than among the defects. When some yttrium (Y) and aluminium (A) atoms exchange positions then these defects are existed in YAG. Generally, cations of Al of B site exchange the position with cation of Y in A site. The electron traps are acted in AD defects and affecting the structural properties. For the especially trivalent lanthanide the doping and undoping of YAG garnets materials are importance for the various properties like luminescence. The favourable chemical and physical properties can be characterized, examples thermal conductivity, complex refraction, high and low frequencies of vibrational and rotational. The best famous garnet is like as YAG ‘*Yttrium Aluminium Garnet*’ ($Y_3Al_5O_{12}$) when Nd^{3+} is dopped in the garnet constitutes, it converted into laser sensitive materials [7]. We have some more garnet structure like (GGG, LuAG) which are mostly used for that types of materials and few lanthanide ions (trivalent ions) can be acted like active centres [8-12]. If discussion takes place for the optical properties with interesting optical materials, then trivalent lanthanide ions play vital role for bulk materials of the garnet families with crystalline and polycrystalline by that some other properties can be studies like material for detector for high energy application [13-14]. The white LED devises and fluorescence thermometry [15-18] may be investigated. Due to this interesting significance, many researchers want to build-up the interest and Nanoscale garnet powder doped with trivalent lanthanide ions can be given favourable and desirable results with efficient. We will discuss these materials which are most interesting materials in this review.

Lanthanide Doped Nanocrystalline Garnets

On the basis of our best knowledge and analysis, this review paper states that the synthesis of garnet crystal doped with guest materials of chimie douce for high thermal insulator was published in 1986 [19]. The researcher uses the sol–gel synthesis method for YAG with suitable stoichiometry in dilute solution. Gels were formed and provide calcination and sintering at 80–85 °C for 12 hours and final we give heating treatment from room temperature to 1550 °C and maintaining constant temperature for 8 hours and the we go with characterization process inclusion of structural characteristics gives information and evidence of particle size with suitable shaping constant, Photoluminescence characterization gives excitation wavelength and emission wavelength trough which we can predict which type of medication is needed for the material which gives desirable results.

The excitation wavelength for the materials is obtained as 335 nm and emission wavelength 492 nm. The excitation goes under the high energy radiation *i.e.*, ultraviolet region and emission in the visible region. But according to most researchers there will be needed some modification up to which the emission wavelength is shifted blue called as blue shift [20]. After more than a decade, the sol-gel method for preparation of product from YAG is appeared which describes explicitly the sample preparation of garnet [21]. The aluminium and yttrium nitrates had been mixed up in the aqueous formation of acid (citric) and giving heating treatment at 80oC for the 20 hours by which we got gels then they provided drying treatment and heat treatment at various temperatures between 700 and 1200 °C for 24 hours.

The product nanoparticle formation was studied by various techniques of characterization which had given the compositional, structural, morphological, topographical studies gives by X-ray powder diffraction method, SEM, and TEM. The particle size was obtained in the range of nanometre [22]. The research with lanthanide (trivalent) doped in garnet nano powders was published firstly in 1999 [23] through which they went via dopant of lanthanide ions in YAG garnet nanomaterials were formed by famous sol-gel nanomaterial synthesis methodology with suitable precursors for aluminium cerium oxide or cerium inorganic salts. During the formation of the material, they used ethylene glycol as complexing agent. While using the inorganic salts, the YAG were formed in nanoparticles by provide heating between 1000 °C to 12000 °C and while using the alkoxide precursors, the YAG were formed in nanoparticles by provide heating between 700 °C to 800 °C for 16 hours.

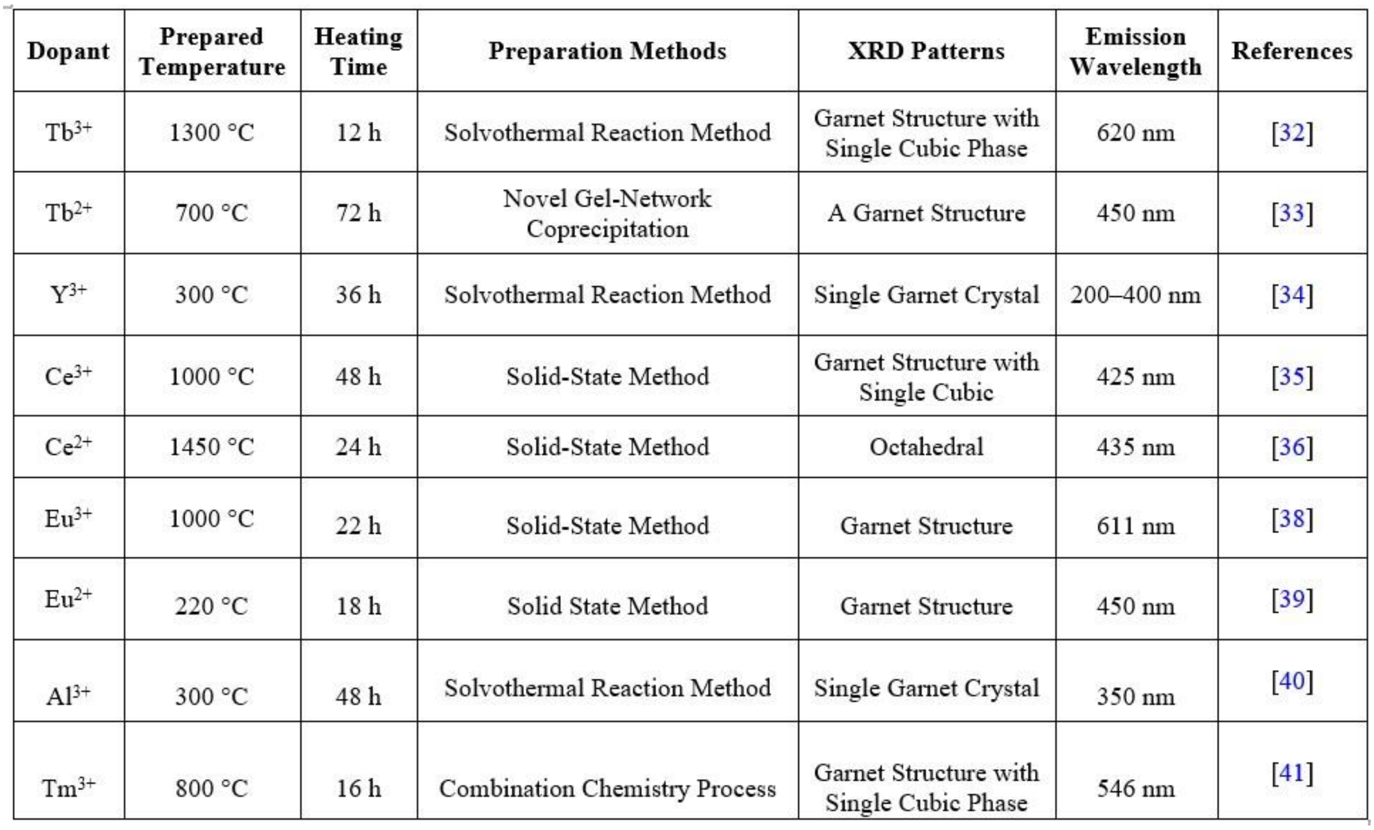
These comparative products were investigated by various instruments like X-ray Diffractometer for determination of particle size and nature of crystal structure with possibility of defects, Scanning electron microscope for topographical and morphological surface study of the materials with grain size and grain boundary of the material. By these characterizations of the materials they could get the particle size of the material in the range of nanoscale (about 70 nm) and they determine crystal structure in the form of simple cubic and the electric conductivity could be obtained by the proper instrument like XPS. Before two decades, the optical spectroscopy for YAG garnet nanoparticle with trivalent lanthanide ions with 5 mol% was studied and published two papers [24]. The materials were synthesized by sol-gel method. The final product in form of gels was provided heating treatment at temperature from 800 to 1000 °C for 26 hours and formation of nanoparticle. The garnet materials doped with proper dopant which gave the interesting result for excitation and emission spectrums. The garnet structure such as YAG oxide doped with Ce^{3+}, got d-f transitions and doped with Nd^{3+}, got f–f transitions. The materials were undergone the calcination and sintering at different temperatures. The characterizations for material were provided for particle size, emission wavelength, rate of agglomeration, bounding lengths among the grains with grain boundaries were done possible by XRD, SEM, TEM, and PL instrumentations [25].

The garnet nanocrystalline materials with doped trivalent Nd in YAG and provide the luminesces characterization to the materials and they were found that the emission transition observed from exited level $^4F_{3/2}$ to $^4F_{5/2}$. The researchers could explain how this transition took place and they gave explanation on the basis of increasing population from high exited energy level to suitable level, due to this transition, affecting on particle size and result was that the particle size reduced. When they gave the laser treatment the transition took place from $^4F_{3/2} \longrightarrow {}^4I_{11/2}$ and they were able to discuss the decay curves which were not exponential curves and decay rate was also not affecting on the structural properties but the heating time and temperature took the part in particle size. This type of materials may be good for laser and solid state polychromatic light production applications because of transparent & glass ceramics [26].

By the literature survey, there is vital scope in this field, also useful applications in white light, laser with transparent ceramics in nanocrystals [27-28]. First paper on frequency response on the garnet material was published in 2003. In that paper, the researchers discussed the preparation and analyzation in optical spectroscopy of the material doped with 1 mol% of Er^{3+} and 5 mol% of Er^{3+}. These materials were gone through investigation of prepared materials by combustion synthesis methodology. It is nothing but propellant preparation. The reaction takes place between metal nitrates and an organic fuel in exothermic process undergoes heating treatment at temperature 500 °C for 1 to 2 hours for decomposing the residual CHD (carbohydrazide) with nitrate dopant [29].

The materials in the form of powder which is studied by X-Ray diffractometer which gives the evidence about crystal structure and particle size in the nano range about 20 nm. They also discuss the Infrared spectroscopy could not be investigated because the sample got undesirable due to moisture & CO_2. Since atmospheric gases are absorbed by the specimen, this is the major affecting on efficiency on the garnet material with doped trivalent lanthanide ions from rare earth materials [30]. The specimen showed the emission spectra in visible region as green, red colour also closed to IR regions. The excitation wavelength were found 488 nm and more significant for anti-stockes emission by Raman spectroscopy in IR region about 800 nm [31]. The other literature survey will be discussed as table 1.

Table 1: The effect of temperatures and preparation methods on crystrual structure and luminensce properties with different cations



Dopant	Prepared Temperature	Heating Time	Preparation Methods	XRD Patterns	Emission Wavelength	References
Tb^{3+}	1300 °C	12 h	Solvothermal Reaction Method	Garnet Structure with Single Cubic Phase	620 nm	[32]
Tb^{2+}	700 °C	72 h	Novel Gel-Network Coprecipitation	A Garnet Structure	450 nm	[33]
Y^{3+}	300 °C	36 h	Solvothermal Reaction Method	Single Garnet Crystal	200–400 nm	[34]
Ce^{3+}	1000 °C	48 h	Solid-State Method	Garnet Structure with Single Cubic	425 nm	[35]
Ce^{2+}	1450 °C	24 h	Solid-State Method	Octahedral	435 nm	[36]
Eu^{3+}	1000 °C	22 h	Solid-State Method	Garnet Structure	611 nm	[38]
Eu^{2+}	220 °C	18 h	Solid State Method	Garnet Structure	450 nm	[39]
Al^{3+}	300 °C	48 h	Solvothermal Reaction Method	Single Garnet Crystal	350 nm	[40]
Tm^{3+}	800 °C	16 h	Combination Chemistry Process	Garnet Structure with Single Cubic Phase	546 nm	[41]

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Conclusion

The phosphor in the garnet components were doped with lanthanide trivalent ions was discussed with some interesting examples in this review paper. Researchers examined the literatures of the said topic in last three to four decades and had been shown that there were suitable sample preparation methods were available, also sufficient instrumentation technology ware provided for the research. Because of that, the researchers had been working in this domain by which they could easily choose the proper stepwise procedure according to availability of the characterizing technology with desired crystal size. The properties of luminesce of the garnet material activated by lanthanide ions were directly related with temperature and heating time. The excitation wavelength was affected by heating time and activated ions which were directly shown in the results. Also, the crystal size varies with heating treatment provided to the sample.

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