Ultraviolet B emission from a Gd^{3+} -doped BaAl_2O_4 powder phosphor

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Abstract. A $\text{BaAl}_2\text{O}_4:\text{Gd}^{3+}$ phosphor was successfully prepared using a combustion technique. An X-ray diffraction pattern was used to characterize the resultant phosphor, and the photoluminescence (PL) of the prepared $\text{BaAl}_2\text{O}_4:\text{Gd}^{3+}$ was studied. Under a 273-nm excitation, the main emission peak of the phosphor is located at 314 nm, and this is attributed to the $^6\text{P}_{7/2} \rightarrow ^8\text{S}_{7/2}$ transition of Gd^{3+} . Electron paramagnetic resonance (EPR) spectrum appears to be U-shaped, and lines are evident at $g_{\text{eff}} \sim 2.14, 4.56$ and 6.75 . The PL and EPR analyses indicate the presence of Gd as Gd^{3+} in this sample.

Keywords. Combustion; EPR; Gd^{3+} ; BaAl_2O_4 ; phosphor; luminescence.

1. Introduction

Oxide materials are important host materials for the study of advanced phosphors due to the ease of their synthesis and their thermal and chemical stabilities. Among the phosphor materials, the rare-earth activated alkaline-earth-aluminate materials have garnered enormous significance due to properties like high stability, long persistent behaviour and high quantum efficiency [1–3]. The alkaline earth aluminates having the general formula MAI_2O_4 ($\text{M} = \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}$ or Mg^{2+}) are widely used as the host lattices for the doping of rare-earth ions [3–6]. Among these aluminates, barium aluminate (BaAl_2O_4) is a material that is widely applied in the field of electronics for devices such as cathode-ray tubes, field-emission displays, plasma display panels and fibre amplifiers [7–10]. Furthermore, BaAl_2O_4 is a high-temperature-resistant material with sound ferroelectric and catalytic properties and hence creating its technological importance [11–13].

The rare-earth- as well as transition-metal-ion-doped BaAl_2O_4 phosphors have been synthesized and investigated throughout the past decade due to their excellent luminescence properties. Singh *et al* [14] reported on the combustion synthesis and luminescence properties of $\text{BaAl}_2\text{O}_4:\text{Mn}^{4+}$, while Suriyamurthy *et al* [15] reported on the luminescence of the $\text{BaAl}_2\text{O}_4:\text{Mn}^{2+}, \text{Ce}^{3+}$ phosphor. A rapid synthesis and enhancement in the down conversion of the emission properties of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{RE}^{3+}$ ($\text{RE}^{3+} = \text{Y}, \text{Pr}$) nanophosphors have been reported by Singh *et al* [16]. Ryu *et al* [17] reported on preparation of the crystalline fibres of codoped

$\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}:\text{Cr}^{3+}$. Vrankić *et al* [18] studied the X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) data of the chromium (Cr)-doped BaAl_2O_4 phosphor.

Ultraviolet (UV)-light sources (200–400 nm) have been proven to significantly used in a variety of applications such as photolithography, UV curing skin diseases, polymerization and chemical reactions [19–22]. According to research, UV type-B (UVB) light emission is suitable for biomedical applications [22–24]. Furthermore, UV light is well-known as a useful tool in medical sterilization treatments for the curing of skin diseases and the generation of vitamins D2 and D3 [25–27]. Since the transition in trivalent gadolinium (Gd^{3+}) ions from its $^6\text{P}_{7/2}$ level to $^8\text{S}_{7/2}$ level provides a narrowband-UVB emission in the region of approximately 312–315 nm [28,29], the Gd^{3+} ion is one of the most suitable activator ion. The activation of phosphor materials with Gd^{3+} ions is a currently attractive practice for the creation of suitable UVB light sources that can be integrated into the designs of the phototherapy lamps that are used in the treatment of skin diseases.

There have been a number of reports on Gd^{3+} -doped UV-emitting phosphors published so far. Jiménez [30] reported an enhanced UV emission of the Gd^{3+} in glass that was achieved using a silver-ion (Ag^+) codoping. Singh *et al* [31] studied UVB emission in the Gd-activated $\text{Y}_4\text{Zr}_3\text{O}_{12}$ phosphor. UV luminescence study in the Gd^{3+} -doped yttrium oxide (Y_2O_3) phosphor has been done by Abdullah *et al* [32]. Mokoena *et al* [33] reported on the luminescence properties and the particle morphology of the $\text{Ca}_3(\text{PO}_4)_2:\text{Gd}^{3+}, \text{Pr}^{3+}$

phosphor. Finally, luminescence and electron paramagnetic resonance (EPR) studies of the $\text{BaZrO}_3\text{:Gd}^{3+}$ phosphor have been reported by Singh *et al* [34].

To obtain the detailed structural information of BaAl_2O_4 , several investigations have been carried out and various spectroscopic methods have been used. To the best of the author's knowledge, previous reports on Gd^{3+} -doped BaAl_2O_4 phosphors have not been published. In consideration of this literature status, a detailed spectroscopic investigation of the Gd^{3+} -doped BaAl_2O_4 phosphor was carried out in the present study using different spectroscopic methods such as XRD, EPR and photoluminescence (PL) study.

2. Experimental

A $\text{Ba}_{0.97}\text{Al}_2\text{O}_4\text{:Gd}_{0.03}$ phosphor was prepared using a solution-combustion technique. To prepare $\text{Ba}_{0.97}\text{Al}_2\text{O}_4\text{:Gd}_{0.03}$, 0.6767 g of barium nitrate ($\text{Ba}[\text{NO}_3]_2$), 2.0 g of aluminium nitrate nonahydrate ($\text{Al}[\text{NO}_3]_3 \cdot 9\text{H}_2\text{O}$), 3.9 g of urea ($\text{CH}_4\text{N}_2\text{O}$), 0.0309 g of boric acid (H_3BO_3) and 0.0361 g of gadolinium nitrate hexahydrate ($\text{Gd}[\text{NO}_3]_3 \cdot 6\text{H}_2\text{O}$) were used. The stoichiometric amounts of the starting materials were placed in a china dish and mixed with the minimum amount of deionized water to perform the combustion reaction. The resultant solution was allowed to react at 95°C for 20 min to obtain a homogeneous solution. Then the solution was introduced into a muffle furnace that had been preheated to 500°C . The products obtained from the combustion process are fluffy masses, and these were crushed into a fine powder using a mortar and pestle. The as-prepared powder was further used for the purpose of characterization.

The XRD spectrum is studied at room temperature (RT) using an X'Pert Pro Diffractometer (PANalytical, The Netherlands) with $\text{Cu-K}\alpha$ radiation in the 2θ range of 10° – 80° . The PL measurements were carried out at RT using the RF-5301PC spectrofluorophotometer (Shimadzu, Japan) equipped with a xenon flash lamp. The EPR spectrum of the phosphor was studied using the FE1X ESR spectrometer (JEOL, Japan) that was operated in the X-band frequencies and with a field modulation of 100 kHz.

3. Results and discussion

3.1 XRD studies

Figure 1 shows the XRD pattern of the $\text{BaAl}_2\text{O}_4\text{:Gd}^{3+}$ phosphor. The samples prepared at 500°C show the main diffraction peaks corresponding to the hexagonal phase of BaAl_2O_4 according to the Joint Committee on Powder Diffraction Standards (JCPDS) file no. 71-1323. In addition, there is a presence of a few minor impurity phases in the samples and they are marked as $\bullet$ and $\blacklozenge$. The impurity peak marked as $\bullet$ belongs to the unreacted $\text{Ba}(\text{NO}_3)_2$, which is one of the precursor materials.

Figure 1. X-ray powder diffraction pattern of the $\text{Ba}_{0.97}\text{Al}_2\text{O}_4\text{:Gd}_{0.03}$ phosphor.

The impurity peak marked as $\blacklozenge$ belongs to the $\text{BaAl}_2\text{O}_{19}$ phase. Mothudi *et al* [35] also reported the same impurity peaks when they prepared BaAl_2O_4 using a combustion method. It has been reported in the literature that the temperature required for the synthesis of BaAl_2O_4 is within the range of 900 – 1300°C [12,17,18]. It is worth mentioning that the hexagonal phase of BaAl_2O_4 was obtained even at a 500°C furnace temperature. The sample XRD patterns indicate that the effect of the small amount of the Gd^{3+} ions on the phase structures is virtually nonexistent. To calculate the crystallite size from the strongest XRD peak (202), the well-known Scherrer equation was applied, as follows: $d = 0.9\lambda / \beta \cos \theta$, where λ is the wavelength of the incident X-rays, θ is the corresponding Bragg's diffraction angle and β is the full width at half maximum (FWHM) of the (202) peak. The crystallite size calculated using this method was found to be 44.21 nm.

3.2 PL studies

Figure 2a shows the excitation spectrum of the $\text{BaAl}_2\text{O}_4\text{:Gd}^{3+}$ phosphor at RT when the emission wavelength was fixed at 314 nm. This spectrum exhibits 6 Gd^{3+} characteristic bands in the UV region. These are centred at 244, 246, 252, 273, 275 and 279 nm [36,37]. These bands have been attributed to the $\text{Gd}^{3+}:4f-4f$ intraconfigurational transitions and the $^8\text{S}_{7/2} \rightarrow ^6\text{D}_J$ and $^8\text{S}_{7/2} \rightarrow ^6\text{I}_J$ transitions [38–42]. The prominent and very sharp peak centred at 273 nm has been attributed to the $^8\text{S}_{7/2} \rightarrow ^6\text{I}_J$ transition. In the PL excitation spectrum, three types of the typical band groups such as $^6\text{P}_J$, $^6\text{I}_J$ and $^6\text{D}_J$ are detectable and these can be associated with the transitions from the ground state of the Gd^{3+} ions to the higher excited states [43–45]. The excited states in the present case are $^6\text{I}_J$ and $^6\text{D}_J$. Gd^{3+} ,

Figure 2. Photoluminescence spectra of the Ba_{0.97}Al₂O₄:Gd_{0.03} phosphor. (a) Excitation spectrum ($\lambda_{\text{emi}} = 314 \text{ nm}$) and (b) emission spectrum ($\lambda_{\text{exi}} = 273 \text{ nm}$).

the ion of choice for the implementation of quantum cutting devices [46,47], features a distance of approximately $32,000 \text{ cm}^{-1}$ between the first excited state ($^6P_{7/2}$) and the ground state ($^8S_{7/2}$), and this is by far the largest among the rare-earth ions. The observed band positions are in good agreement with the band positions reported elsewhere [48]. Shinde *et al* [49] studied UVB-emitting Gd³⁺ phosphors regarding their potential application as phototherapy lamp phosphors.

Figure 2b shows the emission spectrum that was observed in the UV region with a fixed excitation wavelength of 273 nm. The PL emission spectrum exhibited an intense narrow band centred at 314 nm in the UV region that arose due to an electric-dipole transition. This intense band was attributable to the $^6P_{7/2} \rightarrow ^8S_{7/2}$ transition of the Gd³⁺ ions [38]. Especially, the narrowband-UVB emission is of importance in medical phototherapy. In this present study, the sample exhibited a narrow band-UV emission at 314 nm and that could be suitable for the production of phototherapy lamps and useful in curing skin diseases. Also, the FWHM of the UVB emission peak at 314 nm corresponding to the $^6P_{7/2} \rightarrow ^8S_{7/2}$ transition in the BaAl₂O₄:Gd³⁺ phosphor is 2.86 nm. The emission spectrum also exhibited a weak emission band at 308 nm, and this band has been attributed to the $^6P_{5/2} \rightarrow ^8S_{7/2}$ transition. The observed emission-band positions are in good agreement with the emission-band positions that are reported elsewhere [50–52]. Shinde *et al* [49] did not observe any emissions in the visible range, with the UV region showing the only observable emissions; they observed two peaks centred at 308 and 314 nm. As the radiative

transitions occur over a large energy range, nonradiative transitions cannot compete with the radiative transitions [53,54]. Tamrakar *et al* [50] observed an emission line at 312 nm.

3.3 EPR studies

The g values are calculated using the EPR equation [55],

$$h\nu = g\beta B \quad (1)$$

where g is the g factor, h is the Planck's constant, ν is the microwave frequency, β is the Bohr magneton, and B is the magnetic field at the centre of the signals. The g factors have been attributed to the tetrahedral, octahedral or cubic symmetry between the dopant and the host lattice with a moderate distortion. The electronic structure of the rare-earth ions can be studied effectively using the g factors. For the rare-earth ions, the g factors deviate from the free electron value of 2.0023 through the spin–orbit interactions with the phosphor–lattice environment. It is known that Gd belongs to paramagnetic substances and get magnetized when placed in an external magnetic field.

The energy levels of the Gd³⁺ ions in the external magnetic field B are described using the spin Hamiltonian [56,57],

$$H = g_0\beta BS + D[S^2z - 1/3S(S+1)] + E(S_X^2 - S_Y^2) \quad (2)$$

Figure 3. EPR spectrum of the $\text{Ba}_{0.97}\text{Al}_2\text{O}_4:\text{Gd}_{0.03}$ phosphor.

where the first term is the Zeeman term. The second-order terms describe the ligand-field effects and D and E are the axial and rhombic constants of the energy-level splitting in a zero magnetic field, respectively. For the Gd^{3+} , the higher-order terms cannot be neglected. The Gd^{3+} EPR spectra of disordered materials are well described by this spin-Hamiltonian.

The EPR spectrum of $\text{BaAl}_2\text{O}_4:\text{Gd}^{3+}$ at RT is shown in figure 3. This spectrum exhibits resonance signals with the effective g factors of 2.14, 4.56 and 6.75. The resonance signal at the effective g factor of 2.14 has been attributed to the octahedral or tetrahedral symmetry with a moderate distortion [58,59]. The resonance signal at the g factor of 6.75 has been attributed to the cubic-symmetry field with a moderate distortion [58,59]. The resonance signal at the g factor of 2.14 was assigned to the paramagnetic ions in the sites that are characterized by relatively weak ligand fields, wherein the Zeeman term is dominant. The resonance signals with $g > 2.0$ have been attributed to the paramagnetic ions in the sites of the relatively strong ligand field, where the ligand-field terms are comparable with or larger than the Zeeman term [60].

The resonance signal with the effective g factor of 4.56 associated with the Gd ions with a coordination number lower than 6 exhibits a relatively strong ligand field with an orthorhombic symmetry [61]. Rada *et al* [61] studied the EPR spectroscopy of the Gd environment in borate-tellurate glass ceramics. They observed six resonance signals with the effective g factors of 2.0, 2.8, 3.3, 4.3, 4.8 and 6. The resonance signal at the g factor 4.8 has been attributed to a strong ligand field with an orthorhombic symmetry. The resonance signals at the effective g factors of 3.3 and 4.3 have been attributed to the vitreous and disordered polycrystalline materials, respectively. The resonance signals at the g factors of 6.0, 2.8 and 2.0 have been attributed to the cubic, octahedral or tetrahedral symmetry, respectively, with a moderate distortion. Simon *et al* [58] studied the structural properties of the Gd^{3+} ions in bismuth-germanium glasses. They observed the resonance signals with the effective g factors of 6.0, 2.8 and 2.0. These resonance signals have been attributed to the cubic, tetrahedral or octahedral symmetry with a moderate

distortion. The magnetic susceptibility and EPR studies of the Gd^{3+} ions in bismuth-borate glasses have been reported by Ardelean and Griguta [59]. They observed the resonance signals with the effective g factors of 6, 2.87 and 2.0. These resonance signals are attributed to the U-spectrum of the Gd^{3+} ions in disordered materials. Rada *et al* [62] conducted experimental and theoretical studies on the structure of the Gd^{3+} ions in lead-tellurite glasses. They observed the resonance signals with the effective g factors of 3.3 and 4.3 and which have been attributed to vitreous and disordered polycrystalline materials, respectively. The EPR properties of the glasses are similar to those of the phosphors, and therefore it is reasonable to equate the properties of the glasses with those of the phosphors.

It is well documented that the Gd^{3+} comprises a half-filled electronic shell with a $4f^7$ electronic configuration. The ground-state $^8S_{7/2}$ multiplet is characterized by an absence of the orbital moment ($L = 0$) and the value of the spin moment ($S = 7/2$). The eightfold degenerated level of the Gd^{3+} being placed in the BaAl_2O_4 phosphor splits into four Kramers' doublets. The EPR spectrum consists of three resonance signals from one of the seven fine-structure absorption lines that are the results of both the intradoublet and interdoublet transitions. Since the effective spin-quantum number is $S = 7/2$, seven fine-structure lines need to be obtained for the Gd^{3+} . In the present case, the authors observed signals due to a single fine-structure component. The observed spectrum is the most frequent signature of the S -state rare-earth ion in low-symmetry sites [36,63]. The applied magnetic field splits the ground state into eight singlet states so that seven transitions may occur. It is expected that the Gd^{3+} signals can be observed in the range of $g > 2$ if the ligand-field strength is greater than the microwave frequency, whereas if the microwave frequency is of the same order as that of the ligand-field strength, then the zero-field resonance can be seen. However, if the microwave frequency is larger than the ligand-field strength, the signals will be concentrated in the vicinity of a g factor of 2.0 [36,63].

The zero-field splitting (ZFS) parameter (D) can be calculated based on the ΔB values using the following expression [64]:

$$D \approx \Delta B/6. \quad (3)$$

This equation is valid for the first order of the perturbation theory. The calculated D value is 36.75 mT at RT and is consistent with the reported literature value [65,66]. The ZFS parameter arose due to the combined action of the spin-orbit and electronic spin-spin coupling that had been obtained as perturbations on the ligand-field states [67,68].

The EPR spectra of the Gd^{3+} ions are known as the U-spectrum because of their omnipresence in vitreous as well as polycrystalline materials [68–74]. Several explanations of the U-spectrum regarding the Gd^{3+} ions in materials have been given by different authors [70,71]. A detailed analysis of the U-spectrum was previously performed by Nicklin *et al* [71], whereby an extensive search for a single set of 'rhombic'

crystal-field parameters that could simultaneously account for all of the main features of the U-spectrum was conducted; as a result, the feature of a g factor of 6.0 was attributed to a strong cubic-crystal field. Chepeleva *et al* [70] discussed the U-spectrum and attributed the resonances of a g factor of 6.0 to a strong cubic field on the basis of the solutions they obtained for a ‘cubic’ Hamiltonian in the strong crystal-field limit, where the Zeeman interaction may be treated as a perturbation. Antuzevics *et al* [75] studied the ZFS of the Gd^{3+} impurity in scandium fluoride (ScF_3) using the EPR at 77 and 295 K. Their analysis of the ZFS parameters indicated that the local structure of the Gd^{3+} centre expands positively with temperature.

4. Conclusions

A UVB-emitting $BaAl_2O_4:Gd^{3+}$ phosphor was synthesized using a combustion technique in the present study. The XRD pattern confirms that the synthesized sample shows a $BaAl_2O_4$ hexagonal phase. The average crystallite size is 44.21 nm, while the PL under the 273-nm excitation showed sharp intense peaks of a high intensity at approximately 314 nm that have been ascribed to the transition between the excited state ($^6P_{7/2}$) and the ground state ($^8S_{7/2}$) of the Gd^{3+} . The present phosphors can act as the UVB-emitting phosphor for phototherapy lamps. EPR spectrum exhibited resonance signals at the effective g factors of 2.14, 4.56 and 6.75. The ZFS parameter that was obtained from the EPR data is 36.75 mT.

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References

- [1] Lephoto M A, Ntwaeaborwa O M, Pitale S S, Swart H C, Botha J R and Mothudi B M 2012 *Physica B* **407** 1603
- [2] Ravichandran D, Johnson S T, Erdei S, Roy R and White W B 1999 *Displays* **19** 197
- [3] Yamamoto H and Matsuzawa T 1999 *J. Lumin.* **72–74** 287
- [4] Clabau F, Rocquefelte X, Jobic S, Deniard P, Whangbo M H, Garcia A *et al* 2005 *Chem. Mater.* **17** 3904
- [5] Singh V, Rao T K G and Kim D K 2008 *Radiat. Meas.* **43** 1198
- [6] Qiu Z, Zhou Y, Lü M, Zhang A and Ma Q 2007 *Acta Mater.* **55** 2615
- [7] Sun F and Zhao J 2011 *J. Rare Earths* **29** 326
- [8] Xie C, Zeng Q, Dong D, Gao S, Cai Y and Oganov A R 2014 *Phys. Lett. A* **378** 1867
- [9] Pathak P and Kurchania R 2016 *Radiat. Phys. Chem.* **127** 56
- [10] Jia D, Wang X J, Van der Kolk E and Yen W M 2002 *Opt. Commun.* **204** 247
- [11] Dejene F B 2013 *Opt. Mater.* **35** 1893
- [12] Yang G, Li Y and Men Y 2015 *Catal. Commun.* **69** 202
- [13] Zhu Z, Liu F and Zhang W 2015 *Mater. Res. Bull.* **64** 68
- [14] Singh V, Natarajan V and Kim D K 2008 *Radiat. Eff. Defects Solids* **163** 199
- [15] Suriyamurthy N and Panigrahy B S 2007 *J. Lumin.* **127** 483
- [16] Singh D, Tanwar V, Simantilleke A P, Mari B, Kaydan P S and Singh I 2016 *J. Mater. Sci. Mater. Electron.* **27** 2260
- [17] Ryu H and Bartwal K S 2009 *Cryst. Res. Technol.* **44** 69
- [18] Vrankić M, Gržeta B, Lützenkirchen-Hecht D, Bosnar S and Šarić A 2015 *Inorg. Chem.* **54** 11127
- [19] Carbaugh D J, Wright J T, Rajan P, Kaya S and Rahman F 2016 *Thin Solid Films* **615** 423
- [20] Hong X, Wen J, Xiong X and Hu Y 2016 *Chemosphere* **154** 537
- [21] Liang B, Pang D, Jin C, Li F and Wang Y 2012 *Polym. Degrad. Stab.* **97** 2162
- [22] MacKie R M 2000 *Radiat. Prot. Dosim.* **91** 15
- [23] Dogra S and Kanwar A J 2004 *Indian J. Dermatol. Venereol. Leprol.* **70** 205
- [24] Köster W and Wiskemann A 1990 *Z. Hautkr.* **65** 1022
- [25] Reich A and Mędrek K 2013 *Int. J. Mol. Sci.* **14** 8456
- [26] Taofiq O, Fernandes Á, Barros L, Barreiro M F and Ferreira I C F R 2017 *Trends Food Sci. Technol.* **70** 82
- [27] Makarova A M, Pasta S, Watson G, Shackleton C and Epstein E H Jr 2017 *J. Steroid Biochem. Mol. Biol.* **171** 187
- [28] Lowe N J 1992 *Semin. Dermatol.* **11** 284
- [29] Asawanonda P and Klahan S O 2010 *Photomed. Laser Surg.* **28** 679
- [30] Jiménez J A 2015 *Mater. Lett.* **159** 193
- [31] Singh V, Sivaramaiah G, Rao J L and Kim S H 2015 *J. Lumin.* **157** 82
- [32] Abdullah Khairurrijal M, Waris A, Sutrisno W, Nurhasanah I and Vioktalamo A S 2008 *Powder Technol.* **183** 297
- [33] Mokoena P P, Gohain M, Bezuidenhout B C B, Swart H C and Ntwaeaborwa O M 2014 *J. Lumin.* **155** 288
- [34] Singh V, Sivaramaiah G, Rao J L, Watanabe S, Gundu Rao T K, Jagtap S S *et al* 2015 *J. Alloys Compd.* **648** 1083
- [35] Mothudi B M, Lephoto M A, Ntwaeaborwa O M, Botha J R and Swart H C 2012 *Physica B* **407** 1620
- [36] Singh V, Sivaramaiah G, Rao J L and Kim S H 2013 *J. Lumin.* **143** 162
- [37] Singh V, Sivaramaiah G, Rao J L and Kim S H 2013 *Physica B* **416** 101
- [38] Ramteke D D and Gedam R S 2014 *J. Rare Earths* **32** 389
- [39] Moretti F, Chiodini N, Fasoli M, Griguta L and Vedda A 2007 *J. Lumin.* **126** 759
- [40] Miura N, Sasaki T and Matsumoto H 1991 *Jpn. J. Appl. Phys.* **230** L1815
- [41] Alonso P J, Orera V M, Cases R, Alcalá R and Rodríguez V D 1988 *J. Lumin.* **39** 275
- [42] Reisfeld R, Greenberg E, Velapoldi R and Barnett B 1972 *J. Chem. Phys.* **56** 1698
- [43] Deren P J, Strek W and Krupa J C 1998 *Chem. Phys. Lett.* **298** 217
- [44] De Vries A J, Hazenkamp M F and Blasse G 1988 *J. Lumin.* **42** 275
- [45] Binnemans K, Van Deun R, Görller-Walrand C and Adam J L 1998 *J. Non-Cryst. Solids* **238** 11

- [46] Wegh R T, Donker H, Meijerink A, Lamminmäki R J and Hölsä J 1997 *Phys. Rev. B* **56** 1384
- [47] Liu B, Chen Y, Shi C, Tang H and Tao Y 2003 *J. Lumin.* **101** 155
- [48] Binnemans K, Görrler-Walrand C and Adam J L 1997 *Chem. Phys. Lett.* **280** 333
- [49] Shinde V V, Kunghatkar R G and Dhoble S J 2015 *Luminescence* **30** 1257
- [50] Tamrakar R K, Bisen D P and Brahme N 2014 *J. Radiat. Res. Appl. Sci.* **7** 550
- [51] Singh V, Chakradhar R P S, Rao J L, Ledoux-Rak I and Kwak H Y 2011 *J. Mater. Sci.* **46** 1038
- [52] Bosze E J, Hirata G A, Shea-Rohwer L E and McKittrick J 2003 *J. Lumin.* **104** 47
- [53] Dorenbos P 2000 *J. Lumin.* **91** 91
- [54] Zhong J, Liang H, Su Q, Zhou J, Huang Y, Gao Z *et al* 2010 *Appl. Phys. B* **98** 139
- [55] Sivaramaiah G 2016 *Spectroscopic study of materials* (Germany: Lambert), Research Book, ISBN: 978-3-659-88286-9
- [56] Abragam A and Bleaney B 1970 *Electron paramagnetic resonance of transition ions* (UK: Oxford University Press), reprinted 2013
- [57] Griscom D L 1984 *J. Non-Cryst. Solids* **67** 81
- [58] Simon S, Ardelean I, Filip S, Bratu I and Cosma I 2000 *Solid State Commun.* **116** 83
- [59] Ardelean I and Griguta L 2007 *J. Non-Cryst. Solids* **353** 2363
- [60] Culea E, Pop L and Simon S 2004 *Mater. Sci. Eng., B* **112** 59
- [61] Rada S, Dan V, Rada M and Culea E 2010 *J. Non-Cryst. Solids* **356** 474
- [62] Rada S, Culea E and Rada M 2011 *Mater. Chem. Phys.* **128** 464
- [63] Iton L E, Suib S L and Stucky G D 1981 *Bull. Magn. Reson.* **2** 174
- [64] Lipinska Z, Pawlowski M, Zolnierowicz H, Wyszomolek A, Palczewska M, Kaminska M *et al* 2006 *Acta Phys. Pol. A* **110** 243
- [65] Szyzewski A, Lis S, Kruczynski Z and But S 2002 *J. Alloys Compd.* **341** 307
- [66] Brodbeck C M and Iton L E 1985 *J. Chem. Phys.* **83** 4285
- [67] Rudowicz C 1987 *Magn. Reson. Rev.* **13** 1
- [68] Rudowicz C and Misra S K 2001 *Appl. Spectrosc. Rev.* **36** 11
- [69] Iton L E, Brodbeck C M, Suib S L and Stucky G D 1983 *J. Chem. Phys.* **79** 1185
- [70] Chepeleva I V, Lazukin V N and Demdovskii S A 1967 *Sov. Phys. Dokl.* **11** 864
- [71] Nicklin R C, Johnstone J K, Barnes R G and Wilder D R 1973 *J. Chem. Phys.* **59** 1652
- [72] Griscom D L 1980 *J. Non-Cryst. Solids* **40** 211
- [73] Ardelean I, Burzo E, Mitulescu-Ungur D and Simon S 1992 *J. Non-Cryst. Solids* **146** 256
- [74] Sreedhar B, Rao J L, Narendra G L and Lakshman S V J 1992 *J. Phys. Chem. Solids* **53** 67
- [75] Antuzevics A, Rogulis U, Fedotovs A, Berzins D, Voronov V N and J Purans 2015 *Phys. Scr.* **90** 115801