

LaVO₄, LaPO₄ and LaBO₃: synthesis, Rietveld refinement, and comparison of optical properties

G. ÇELİK GÜL*, F. KURTULUŞ

Department of Chemistry, Balikesir University, 10145, Balikesir, Turkey

Rare earth metals luminescent materials have been practically applied in almost all devices from cathode ray tubes to coating materials. Lanthanum containing samples of orthovanadate, orthophosphate and orthoborate (LaVO₄, LaPO₄ and LaBO₃) compounds have been successfully prepared by microwave-assisted solid state synthesis (MASS) method. Characterizations were done by powder X-ray diffraction (XRD), Rietveld refinement method, fourier transform infrared (FTIR) spectroscopy, photoluminescence spectroscopy (PL) and scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS). The Rietveld refinement analyses by using XRD data reveal that LaVO₄ and LaPO₄ powders are crystallized in monoclinic system; LaBO₃ is in orthorhombic. The morphological results confirm the particle sizes are in the range micron to nano-scale. While LaPO₄ and LaBO₃ powders exhibit green phosphor, LaVO₄ seems yellow under visible range.

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1. Introduction

Luminescent materials especially containing rare earth metals have remarkable applicable in almost all devices such as X-ray detectors, lamps, cathode tubes [1], biomedical sensors and markers [2,3]. The complex relationships between structure, properties and stoichiometry must be well-understood to produce oxides [4]. Having the general formula RAO_4 (R =rare earth metal, A =V, P, Ta, W etc.) rare earth compounds have been intensively emphasized for their physical and chemical properties [5]. This typical formula provides flexibility for cation substitution on both R and B sites [6]. The coordination number of R varies from structure to structure and there are wide variations in R–O distances within a given polyhedron [7]. There are different kind of phosphor materials based on lanthanides, such as oxides, silicates, aluminates, vanadates, phosphates and borates [8]. The reason of intensive study about lanthanide cations is exhibition photo luminescent properties due to a wide range of emission colors which are based on $4f-4f$ or $5d-4f$ transitions [1]. A group of them is rare earth orthovanadates and orthophosphates which have been revealed born of top level to apply cathode luminescent, low temperature transformations and Jahn-Teller distortion except a few of them. Besides, these compounds create wide practical field such as laser hosts, sensors and catalyst due to multiple transition of rare earths and electronic structure [9]. Lanthanide orthovanadates are major compounds in this system and exhibit both physical, magnetic and crystallographic properties [10]. Lanthanide

orthovanadates have two crystalline form: monoclinic monazite type and tetragonal zircon type [25,26]. In general, the larger lanthanide ion prefers monazite type owing to its higher oxygen coordination number compared to the zircon type [10]. Lanthanum is the first element of lanthanides with the largest atomic radii naturally should choose monazite type, but as an exception lanthanum prefers more stable zircon type [11]. Tetragonal lanthanum orthovanadate was first synthesized by Ropp and Carroll [12] as a low-crystalline form via conventional route. The corrections about some contradictory reports [13] confirmed that to obtain high crystalline form the soft chemical methods become compulsory, and are used in many researches [14]. In terms of features, lanthanum vanadates and phosphates are promising candidates as phosphor material according to Yan's research [15]. These functional groups have ease charge transfer which make them as potential pigments and photocatalytic material [16]. Lanthanide orthovanadates are candidates on solar energy harvesting due to red shift in the excitation spectra. Low stability of orthovanadates and orthophosphates restrict their application in many fields, although all advantages [17]. Hence, lanthanum phosphates and lanthanum borates have been needed to investigate and compare to orthovanadates. The former lanthanum phosphates have the same crystal structure as lanthanum orthovanadates and exhibit dominant protonic conduction and high chemical stability [18]. Further, lanthanum phosphates have been chosen due to their potential applications on fluorescent lamps and color TV monitors [19]. The latter lanthanum borates are crystallized in

orthorhombic aragonite-type structure with space group Pnam, isomorphs with CaCO₃, and display high temperature protonic conduction, excellent thermal and chemical stability, and high vacuum ultraviolet transparency [20]. On the other hand, RBO₃ (R=rare earth metal) type anhydrous orthoborate compounds have been attracted a great interest for the preparing due to structural complexity because boron atoms to form all kinds of borates planar BO₃, nonplanar BO₃ and tetrahedral BO₄ groups [21]. Many metal borates display important practices in nonlinear optical and laser applications. They have also significant magnetic, catalytic and phosphorescent properties [22]. Due to the mentioned applications, the metal borates find many technological practices in the industrial area.

The leadable high-temperature solid state reaction which alternates the structure is a common method to synthesis rare earth phosphor materials. For the rest, hydrothermal method and chemie douce have been used as wet methods [23]. The related methods have some disadvantages: high reaction temperature, limited homogeneity, complexity and high cost [24]. Therefore, improving a simple and low cost method is an essential necessity. Microwave assisted–solid state synthesis (MASSS) can be an alternative method to obtain these types of compounds. MASSS shorten high temperature heating process, improve yield, and accelerate reaction time and most importantly reducing costs.

From the literature to the best of our knowledge, it is not possible to find any comparatively publications about microwave–assisted synthesis, structural and luminescent properties of lanthanum vanadates, phosphates and borates. In this paper, we present the MASS synthesis of LaVO₄, LaPO₄ and LaBO₃ compounds, comparison of characteristic properties such as: structural, morphological, thermal and luminescent. XRD, FTIR, SEM/EDS and PL of the all compounds have been used as characterization techniques to complete the comparison.

2. Experimental section

All chemical lanthanum (III) oxide, vanadium (V) oxide, phosphorus (V) oxide, and boron trioxide have been used analytical grade, and provided by Merck. LaVO₄, LaPO₄ and LaBO₃ compounds were fabricated using a domestic microwave oven as described conditions: 850 W, 20 min. and 2.45 GHz. In terms of being an example, lanthanum orthovanadate has been synthesized as follows: lanthanum (III) oxide and vanadium (V) oxide in 1:1 molar ratio were weighted and homogenized in an agate mortar. Then, the mixture was laid along porcelain crucible, and treated microwave irradiation. After cooling down to room temperature, the mixture was regrounded, and crystallized at 450 °C for 2 h to obtain best shaped crystals. The same procedure was applied to obtain the

other two compounds. The structural characterizations of LaVO₄, LaPO₄ and LaBO₃ compounds were carried out powder X-ray diffraction (XRD) measurements using Panalytical X'Pert Pro Diffractometer and Cu K_α radiation ($\lambda=1.54056 \text{ \AA}$, 40 mA, 50 kV) with a scan rate of 1°/min with step size 0.02°. The Rietveld analyses of the samples were done by using the High Score Plus (HS+) Program (License number: 92000029). Fourier transform infrared spectroscopy (FTIR) was achieved on a Perkin Elmer Spectrum 100 FTIR Spectrometer from 4000 to 650 cm⁻¹. The morphological properties and chemical compositions of the samples were determined by means of SEM JEOL 6390-LV scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS). The luminescence properties were measured by Andor Solis Sr 500i spectrophotometer (VUV-PL) at grating 1200 and 100 μm slit conditions. Siemens V12 domestic microwave oven and Protherm conventional furnace were used wave and heat treatment, respectively.

3. Results and discussion

The structural properties of LaVO₄, LaPO₄ and LaBO₃ compounds have been studied using XRD spectra which are showed in Fig. 1. All diffractograms show only characteristic diffractions of LaVO₄, LaPO₄ and LaBO₃ compounds and these peaks collaborate with ICSD card numbers 008-8294, 007-9747 and 003-5535, respectively. Other peaks belonging to lanthanum (III) oxide, vanadium (V) oxide, phosphorus (V) oxide, and boron trioxide are not observed in the patterns. All the peaks have been marked as related miller planes in Fig. 1. The observed and calculated “d” values of the compounds are given in Table 1, and the unit cell parameters of the compounds have been calculated by using these values via Rietveld Refinement Program (Table 2). The calculated unit cell parameters nearly agree with the card data.

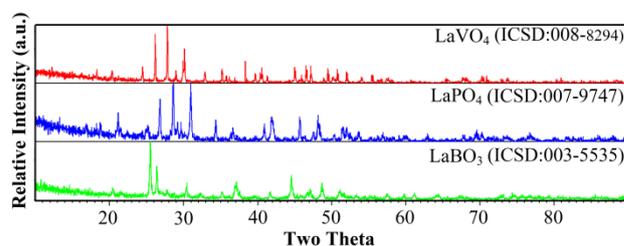


Fig. 1. Powder X-ray diffraction pattern of LaVO₄, LaPO₄ and LaBO₃ compounds

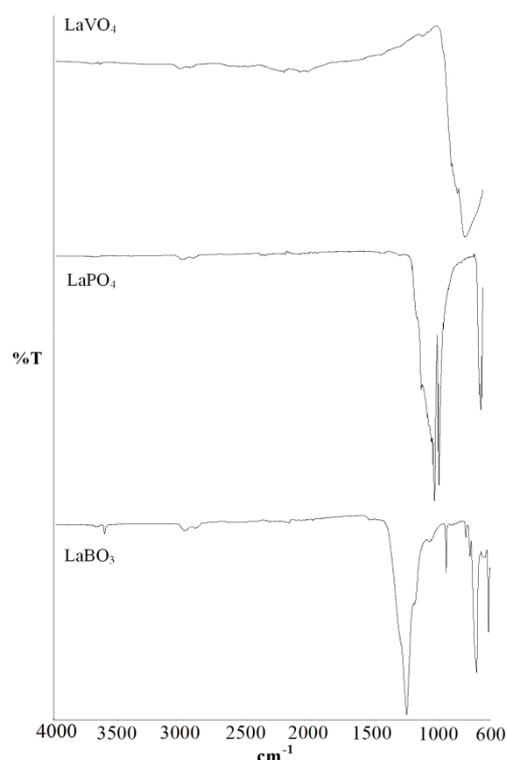
Table 1. The observed and calculated XRD data of LaVO_4 , LaPO_4 and LaBO_3 compounds

LaVO_4			LaPO_4			LaBO_3		
$d_{\text{obs.}}$ (Å)	$d_{\text{calc.}}$ (Å)	h k l	$d_{\text{obs.}}$ (Å)	$d_{\text{calc.}}$ (Å)	h k l	$d_{\text{obs.}}$ (Å)	$d_{\text{calc.}}$ (Å)	h k l
5.4484	5.4443	1 0 0	5.2217	5.2245	1 0 0	4.3637	4.3359	0 1 1
4.8424	4.8431	1 1 -1	4.8437	4.8442	0 1 1	3.5042	3.4900	1 1 1
4.3597	4.3590	1 1 0	4.7140	4.7159	1 1 -1	3.3906	3.3757	1 0 2
4.1887	4.1897	1 0 -2	4.2005	4.2013	1 1 0	2.9400	2.9408	2 0 0
3.6345	3.6375	0 2 0	4.1347	4.1360	1 0 -2	2.5650	2.5486	0 2 0
3.6293	3.6307	1 1 -2	3.5693	3.5697	1 1 -2	2.4383	2.4337	2 1 1
3.4005	3.4010	0 0 2	3.5355	3.5340	0 2 0	2.4351	2.4148	1 0 3
3.2055	3.2077	0 2 1	3.3243	3.3260	0 0 2	2.3990	2.3940	0 1 3
3.0801	3.0810	0 1 2	3.1647	3.1655	2 0 -2	2.1819	2.1677	0 2 2
2.9864	2.9852	2 1 -1	3.1216	3.1209	0 2 -1	2.0456	2.0339	1 2 2
2.9642	2.9639	2 1 -2	3.0866	3.0858	1 2 -1	1.9567	1.9450	1 0 4
2.7241	2.7224	2 0 0	3.0084	3.0094	0 1 2	1.9328	1.9259	2 2 0
2.5509	2.5498	2 1 0	2.8886	2.8890	2 1 -2	1.8754	1.8754	2 2 1
2.5099	2.5104	2 1 -3	2.8789	2.8796	2 1 -1	1.7879	1.7863	3 1 1
2.2701	2.2718	1 3 -1	2.6109	2.6122	2 0 0	1.7723	1.7704	3 0 2
2.2352	2.2340	3 0 -2	2.4672	2.4675	2 1 -3	1.6108	1.6025	0 2 4
2.2235	2.2234	1 1 2	2.4492	2.4502	2 1 0	1.5557	1.5461	1 2 4
2.1863	2.1875	1 2 -3	2.2088	2.2080	1 3 -1	1.4581	1.4540	4 0 0
2.0125	2.0132	2 1 -4	2.1589	2.1596	3 0 -2	1.4546	1.4482	3 2 2
1.9717	1.9727	1 3 1	2.1525	2.1535	1 1 2	1.3038	1.2969	2 3 3
1.9480	1.9487	2 3 -1	2.1454	2.1455	1 2 -3	1.2733	1.2735	4 2 0
1.9235	1.9242	0 2 3	1.9843	1.9847	2 1 -4	1.2585	1.2586	4 2 1
1.8404	1.8402	2 2 1	1.9117	1.9115	1 3 1	1.2456	1.2447	2 0 6
1.7956	1.7966	2 3 3	1.8876	1.8873	2 3 -1	1.2298	1.2248	3 1 5
1.6962	1.6957	2 0 2	1.8778	1.8782	0 2 -3	1.1674	1.1692	2 4 0
1.6232	1.6241	3 2 0	1.8173	1.8118	3 2 -3	1.1249	1.1248	2 4 2

Table 2. Crystal system and unit cell parameters of LaVO_4 , LaPO_4 and LaBO_3 compounds calculated by Rietveld refinement method using X-ray powder diffraction data

Compound	Crystal system	Unit cell parameters		
		a (Å)	b (Å)	c (Å)
LaVO_4	monoclinic	6.7161	7.2759	8.3003
LaPO_4	monoclinic	6.5047	7.0678	8.2822
LaBO_3	orthorhombic	5.8808	5.0965	8.2428

The FTIR spectra of LaVO_4 , LaPO_4 and LaBO_3 compounds are shown in Fig. 2. The vibrations of LaVO_4 in the range of $631\text{-}970\text{ cm}^{-1}$ are correspond to V-O, V-O-V and V=O subgroups of vanadate structure [25]. In the LaPO_4 spectrum, the peaks at $690\text{-}700\text{ cm}^{-1}$, $1000\text{-}1050\text{ cm}^{-1}$, $1100\text{-}1138\text{ cm}^{-1}$ and $1180\text{-}1300\text{ cm}^{-1}$ are related to $\nu_s(\text{PO}_4)$, $\nu_3(\text{PO}_4)$, $\nu_s(\text{OPO})$ and $\nu_{as}(\text{OPO})$ vibrations, respectively. In the third spectrum the peaks at $600\text{-}680\text{ cm}^{-1}$, $700\text{-}900\text{ cm}^{-1}$, $900\text{-}1000\text{ cm}^{-1}$ and $1000\text{-}1300\text{ cm}^{-1}$ are belong to in order $\delta_{di}(\text{BO}_3)$, $\delta_{dd}(\text{BO}_3)$, $\nu_1(\text{BO}_3)/\nu_s(\text{BO}_3)$ and $\nu_{as}(\text{BO}_3)$ of LaBO_3 compound [26].

Fig. 2. The FTIR spectra of LaVO_4 , LaPO_4 and LaBO_3 compounds

In Fig. 3 SEM micrographs of LaVO₄, LaPO₄ and LaBO₃ compounds are demonstrated. Fig. 4 is EDS results of the related compounds. Although homogeneous views of all samples are nearly similar, particle sizes are

changing nm to μm scale. While the particle size of lanthanum vanadate is about in 1-10 μm , dimensions of LaPO₄ and LaBO₃ powders are in nm scale.

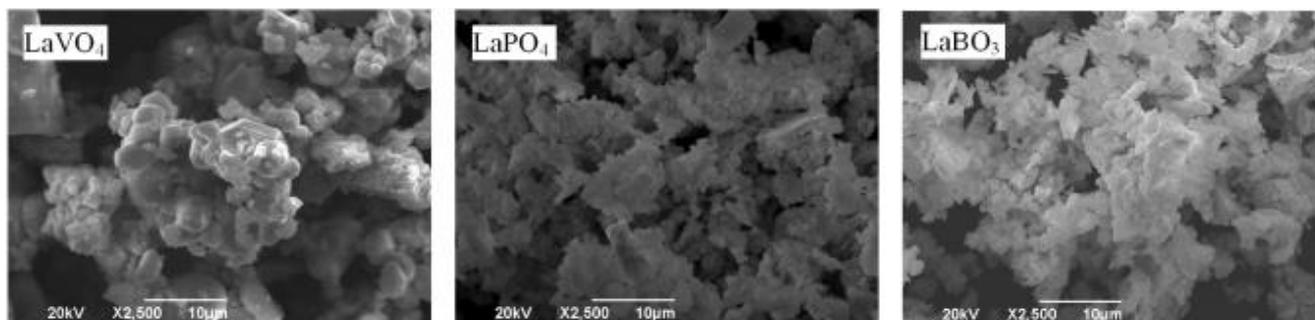
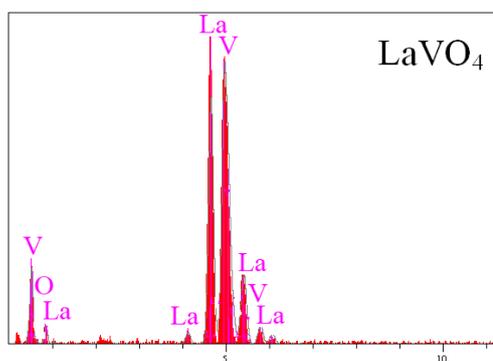
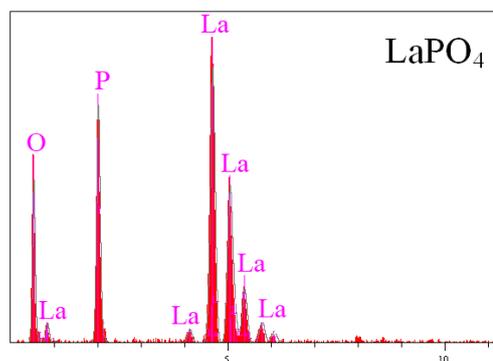


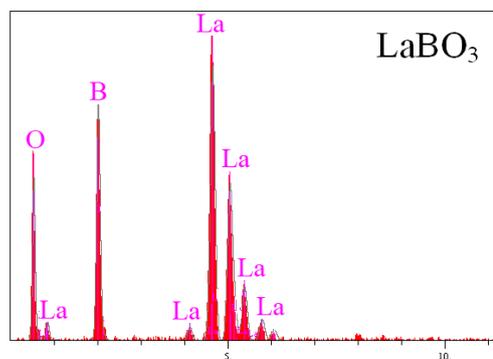
Fig. 3. Scanning electron micrograph images of LaVO₄, LaPO₄ and LaBO₃ compounds



Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units	
O	Ka	9.74	0.987	6.033	wt.%	
V	Ka	137.49	3.708	17.462	wt.%	
La	La	138.83	3.726	76.505	wt.%	
				100.000	wt.%	Total



Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units	
O	Ka	53.43	2.311	18.022	wt.%	
P	Ka	96.85	3.112	11.130	wt.%	
La	La	145.39	3.813	70.847	wt.%	
				100.000	wt.%	Total



Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units	
B	Ka	9.19	0.959	24.366	wt.%	
O	Ka	50.12	2.239	12.672	wt.%	
La	La	193.12	4.394	62.962	wt.%	
				100.000	wt.%	Total

Fig. 4. The results of energy dispersive spectroscopy of LaVO₄, LaPO₄ and LaBO₃ compounds

In Fig. 5, PL emissions of LaVO_4 , LaPO_4 and LaBO_3 compounds are exhibited via black, red and green lines, respectively. In the black line, there are two transitions at 550-650 nm and 650-700 nm which are attributed to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions, respectively [27]. The broad red line is related to several d-f transitions of the lanthanum phosphate [28]. The green line has two bands; first is broad band which display transitions of excited 5d states to the $^2\text{F}_{5/2}$ ground state, and last is small band related to $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition [27,28].

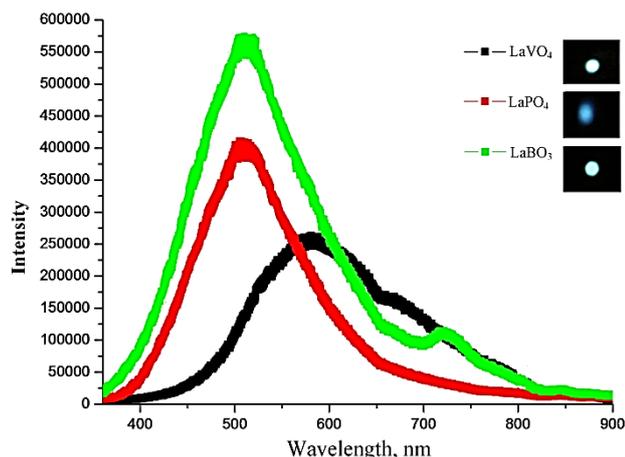


Fig. 5. Photoluminescent spectrum of LaVO_4 , LaPO_4 and LaBO_3 compounds

4. Conclusion

The green or yellow-emitting phosphors LaVO_4 , LaPO_4 and LaBO_3 have been synthesized for the first time microwave-assisted solid state method by using oxides of all elements. The observed XRD data as “d” values have been compared to calculated “d” values by Rietveld refinement method. Also, unit cell parameters of LaVO_4 , LaPO_4 and LaBO_3 compounds have been calculated and crystal systems have been determined Rietveld refinement method. The vibrations in FTIR spectrums confirm the functional groups in the related compounds. The morphological images exhibit that the approximate particle size of lanthanum vanadate is 1-10 μm , meantime dimensions of LaPO_4 and LaBO_3 powders are in 1-10 nm. The luminescent emissions of LaVO_4 , LaPO_4 and LaBO_3 powders are yellow, blue/green and green colors.

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*Corresponding author: gulsahcelik@balikesir.edu.tr