Fabrication of Microcrystalline NaPbLa(WO₄)₃:Yb³⁺/Ho³⁺ Phosphors and Their Upconversion Photoluminescent Characteristics

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Abstract New triple tungstate phosphors NaPbLa(WO₄)₃:Yb³⁺/Ho³⁺ (x = Yb³⁺/Ho³⁺ = 7, 8, 9, 10) were successfully fabricated by microwave assisted sol-gel synthesis, and their structural and frequency upconversion (UC) characteristics were investigated. The compounds crystallized in the tenragonal space group *I*4₁/*a* and the NaPbLa(WO₄)₃ host has unit cell parameters *a* = 5.3927(1) and *c* = 11.7961(3) Å, *V* = 343.05(2) Å³, *Z* = 4. Under the excitation at 980 nm, the phosphors have yellowish green emissions, which were derived from the intense ${}^{5}S_{2}/{}^{5}F_{4} \rightarrow {}^{5}I_{8}$ transitions of Ho³⁺ ions in the green spectral range and the strong ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ transitions in the red spectral range. The optimal Yb³⁺:Ho³⁺ ratio was revealed to be x = 9, which was attributed to the quenching effect of Ho³⁺ ions, as indicated by the composition dependence. The UC characteristics were evaluated in detail under consideration of the pump power dependence and Commission Internationale de L'Eclairage chromaticity. The spectroscopic features of Raman spectra were discussed in terms of superposition of Ho³⁺ luminescence and vibrational lines.

Key words yellowish green phosphor, triple tungstate, microwave assisted sol-gel, upconversion characteristics

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1. Introduction

Recently, upconversion (UC) phosphors, due to unique emission properties and stable crystal structures, have led to the highly attractive characteristics in such important fields of optoelectronics as laser materials, display devices, 3D-assisted LED, solar cell structures, and biological sensors.¹⁻⁵⁾

The double alkaline-earth tungstates with general composition $MLn_2(WO_4)_4$ (M: alkalineearth bivalent metal ion, Ln: trivalent rare-earth ions) belong to the scheelite structured compounds. Recently, the related double molybdates were considered for their highly modulated structures and specific spectroscopic characteristics, including excellent UC emissions.^{6, 7)} In particular, the Na-containing double tungstates NaLn(WO₄)₂ (Ln³⁺ = Gd³⁺, Y³⁺, La³⁺) crystallized in tetragonal phase with the space group *I*4₁/*a* and belong to the scheelite-type structure family. It is well known that the Ln³⁺ ions in the disordered tetragonal structure can be partially substituted by Yb³⁺ and Ho³⁺ ions in the Ln³⁺ sites. The lanthanide trivalent ions could be partially incorporated into the tetragonal scheelite-type structure due to similar ionic radii and that provides a great potential for UC properties in the stable phase.⁸⁻

Concerning lanthanide activator doping for creation of UC phosphors, the Ho³⁺ ions are extremely promising as luminescent centers, while Yb³⁺ ions can be employed as a helpful sensitizer due to their appropriate energy level structure. The Yb³⁺ and Ho³⁺ co-doped UC phosphors are characterized by substantially enhanced UC efficiency because of efficient energy transfer (ET) process from sensitizer to activator, namely, from Yb³⁺ to Ho³⁺. In the UC process, Ho³⁺ exhibits the intense ${}^{5}S_{2}/{}^{5}F_{4} \rightarrow {}^{5}I_{8}$ transitions in the green emission range and the strong ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ transitions in the red emission range enhanced at optimal x =

Yb³⁺/Ho³⁺ values.¹¹⁻¹³⁾ In the past, the rare-earth doped double tungstates NaLn(WO₄)₂ were synthesized by several processes.¹⁵⁻¹⁷⁾ To have a possibility for optimal material selection in laser and photonic fields, it is required to design and synthesize new complex tungstate compounds with stable crystal structures and excellent UC luminescent properties. However, the spectrum of known triple tungstates is relatively narrow and active search for new materials in this field is topical. Among the present technological methods, microwave-assisted synthesis has its advantages of a very short reaction time, homogenous particles, narrow distribution of particle size and high purity of final product.^{18, 19)} The microwave assisted sol-gel (MAS) process can provide efficient results in the synthesis of complex oxide compounds, providing highly homogeneous particle morphology and very stable structures.

In the present work, the triple tungstates based on NaPbLa(WO₄)₃ with the proper doping by Yb³⁺ and Ho³⁺ at x = 7, 8, 9, 10 were successfully fabricated by the MAS based process in the air. The crystal structures of the NaPbLa(WO₄)₃:Yb³⁺,Ho³⁺ solid solutions were obtained by Rietveld analysis for the first time. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed to evaluate the microcrystal morphology. The pump power relationship and Commission Internationale de L'Eclairage (CIE) chromaticity parameters of the UC emission were comparatively evaluated in detail. The optical characteristics were examined using photoluminescence (PL) emission and Raman spectroscopy.

2. Experimental Procedure

In this experiment, the fabrication of triple tungstates of NaPbLa(WO₄)₃ with the proper doping of Yb³⁺ and Ho³⁺ at x = 7, 8, 9, 10 was carried by the MAS method. Na₂WO₄·2H₂O, Pb(NO₃)₂, La(NO₃)₃·6H₂O, (NH₄)₆W₁₂O₃₉·xH₂O in purity of 99.0%, and Ho(NO₃)₃·5H₂O Yb(NO₃)₃·5H₂O in purity of 99.9% were received from Sigma-Aldrich, USA. In addition, citric acid in purity of 99.5% was purchased from Daejung Chemicals, Korea. Besides, distilled water, ethylene glycol (A.R.) and NH₄OH (A.R.) were used to prepare the triple tungstate compounds.

The compounds of Na₂WO₄·2H₂O₂ (NH₄)₆W₁₂O₃₉·xH₂O and Pb(NO₃)₂ were dissolved in 450 mL Pyrex glass with addition of 20 mL of ethylene glycol and 80 mL of 8M NH₄OH, and stirred vigorously under heating. Subsequently, Ho(NO₃)₃·5H₂O, Yb(NO₃)₃·5H₂O and

La(NO₃)₃·6H₂O were dissolved in 450 mL Pyrex glass with addition of citric acid (the molar ratio for citric acid to total metal ions is 2:1) and 100 mL of distilled water and stirred vigorously under heating. The reagents were precisely weighed in accordance with the nominal composition of the samples. The abbreviated notations of NaPbLa(WO₄)₃:Yb³⁺/Ho³⁺ samples are given in Table 1.

Then, the two solutions were combined together and stirred vigorously under heattreatment at 80-100°C. After few minutes, the transparent pure solutions indicated the formation of perfect sol state. It should be adjusted to pH=7-8 by addition of NH₄OH. Then, the stirring was performed under heat-treatment at 80-100°C. For the efficient MAS process in a 450 mL Pyrex glass, the appropriate solution amount is 180-200 mL. The final solutions were highly transparent. For the MAS process, a unique microwave oven was operated at a frequency of 2.45 GHz with the maximum output power of 1250 W for 30 min. The prepared solutions were inserted into the oven with two kinds of cyclic working steps. At the first step, the microwave process was controlled by the cyclic regime of 40 s on and 20 s off for 15 min. At the second step, the further treatment was followed by the cyclic regime of 30 s on and 30 s off for 15 min. After the MAS process, the resultant sols were treated under ultrasonic radiation for 10 min to reach light yellowish transparent sols. Then, the sols were dried at 120°C in a dry oven for one week. The resultant black dried gels were ground and annealed at 850°C for 16 h in the air. After annealing process, white particles were obtained for the pure sample of NaPbLa(WO₄)₃ and pink particles were obtained for the doped compositions of NaPbLa(WO₄)₃:Yb³⁺/Ho³⁺.

The X-ray diffraction patterns for the synthesized powder samples were recorded using XRD (D/MAX 2200, Rigaku, Japan). The microstructural morphology of the synthesized particles was observed using SEM (JSM-5600; JEOL; Japan). The PL spectra were recorded using a spectrophotometer Perkin Elmer LS55 (UK) at room temperature. The pump power relationship of the UC emission intensity was measured at working power from 20 to 110 mW. The Raman spectra measurements were carried out using a LabRam Aramis (Horiba Jobin-Yvon; France) with the spectral resolution of 2 cm⁻¹. The 514.5-nm line of an Ar ion laser was used as an excitation source and the power on the samples was kept at the 0.5 mW level to avoid the sample decomposition.

3. Results and Discussion

The XRD pattern measured for NPLW is shown in Figure 1 and the patterns of doped samples are shown in Figures S1-S4 (Supporting Information). All peaks of powder patterns recorded from NaPbLa_{1-x-v}(WO₄)₃: xHo^{3+} , yYb^{3+} (x = 0, 0.05; y = 0, 0.35, 0.4, 0.45, 0.5) compounds were successfully indexed by the tetragonal cell $(I4_1/a)$ with cell parameters close to those of PbMoO₄²⁰. Therefore, the crystal structure of PbMoO₄ was taken as a starting model for Rietveld refinement. The site of Pb²⁺ ion was considered as occupied by Pb, Na, La, Ho and Yb ions (Figure 2) with fixed occupations according to the suggested formulas. The refinements were stable and gave low R-factors (Table S1, Figures 1, S1-S4). The coordinates of atoms and the main bond lengths are summarized in Tables S2 and S3, respectively. The crystallographic data are deposited in Cambridge Crystallographic Data Centre (CSD # 1948871-1948872). The data can be downloaded from the site (www.ccdc.cam.ac.uk/data_request/cif).

The cell volume dependence on the average ion radius of big cations IR(Na/Pb/La/Ho/Yb), excluding W^{6+} , in the NPLW:Ho³⁺,Yb³⁺ compounds is shown in Figure S5. The IR values were calculated on the base of nominal compositions and the known system of ion radii²¹. It is evident that the cell volume linearly decreases with the IR(Na/Pb/La/Ho/Yb) decrease or the (x + y) increase. This clearly proves the suggested chemical formulas of solid solutions NPLW:Ho³⁺,Yb³⁺. Besides, it is very interesting to see the position of NPLW:Ho³⁺,Yb³⁺ compounds among other known scheelite-type tungstates. In Figure S6, the cell volume of selected simple and complex scheelite-type tungstates is shown as a function of big cation ion radius (IR), where, for the complex tungstates, the average big cation radius is calculated on the base of available structural information [1-15 Supporting Information]. From Figure S6 and Table 4S, it is evident that the unit cell volumes of NPLW:Ho³⁺,Yb³⁺ compounds are in excellent relation to the general trend in scheelite-type tungstates.

The SEM images of synthesized (a) NPLW, (b) NPLW:Yb0.35Ho0.05, (c) NPLW:Yb0.40Ho0.05, (d) NPLW:Yb0.45Ho0.05 and (e) NPLW:Yb0.50Ho0.05 particles are shown in Figure 3. Most of the synthesized samples show similar morphological features with particle size of 2-5 μ m. No difference was observed in particle morphologies shown in Figure 3(a)-(e) and that shows the homogeneous crystallization. Commonly, the agglomerated particles seem to be induced by the atomic interactions between the grains. Therefore, the MAS method, employed to the triple tungstates in the present experiment,

provides the efficient energy transfer to synthesize the uniform NPLW:Ho³⁺,Yb³⁺ triple tungstate compounds and the homogeneous particles with a fine morphology can be efficiently fabricated.

In Figure 4, the UC emission spectra of NPLW:HoYb samples are shown. Under the excitation at 980 nm, the doped samples of NPLW:HoYb exhibited a yellowish green emission composed of red and green emission bands. At the red and green wavelengths, the Ho³⁺ ions show strong transitions ${}^5F_5 \rightarrow {}^5I_8$ and ${}^5S_2/{}^5F_4 \rightarrow {}^5I_8$, respectively. In the UC intensity competition between the samples, the NPLW:Yb0.45Ho0.05 particles provides the strongest 545-nm and 655-nm emission bands. Other samples in emission intensity are in the order of NPLW:Yb0.35Ho0.05, NPLW:Yb0.40Ho0.05 and NPLW:Yb0.50Ho0.05. Thus, the optimal Yb³⁺:Ho³⁺ ratio is revealed to be 9:1, which is attributed to the quenching effect of Ho^{3+} ions at y > 0.45. The logarithmic dependences of the UC intensities at 545 and 655 nm as a function of working pump power over the range of 20-110 mW in the representative sample of NPLW:Yb0.45Ho0.05 are shown in Figure 5. As for the UC process, the slope value (n) for the irradiation pumping power is proportional to the UC emission intensity, where n is the pumping photon number, which are required for the development of UC emission. The UC intensity (I) is proportional to the *n*th power of input pump power (P), which ascribed as $I \propto P^n$. Concerning the dependencies given in Figure 5, the calculated slope value is n = 1.87 in green emission at 545 nm, and n = 1.91 in red emission at 655 nm. Consequently, these dependences could be ascribed to the multi-step energy transfer process, more specifically, two-step process, for the UC mechanism in NaPbLa₁₋ $_{x}(Ho,Yb)_{x}(WO_{4})_{3}$ phosphors.²²⁻²⁴⁾

In Figure 6, the calculated chromaticity coordinates (x, y) and chromaticity locations in CIE map are shown for the synthesized NaPbLa_{1-x}(Ho,Yb)_x(WO₄)₃ phosphors. The individual emission chromaticity points in CIE map are related to the (a) NPLW:Yb0.35Ho0.05, (b) NPLW:Yb0.40Ho0.05, (c) NPLW:Yb0.45Ho0.05 and (d) NPLW:Yb0.50Ho0.05 samples, as defined by color legend given in Fig. 6(B). The calculated chromaticity coordinates x = 0.359 and y = 0.491 for (a), x = 0.357 and y = 0.471 for (b), x = 0.355, y = 0.561 for (c), and x = 0.352 and y = 0.389 for (e) are correspondent to the yellowish green emissions attributed to the intense of ${}^{5}S_{2}/{}^{5}F_{4} \rightarrow {}^{5}I_{8}$ and ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ transitions of Ho³⁺ ions in the NPLW host.

The unpolarized Raman spectrum obtained at room temperature from NPLW sample is shown in Figure S7. It can be divided into three parts: 950-700 cm⁻¹, 425-275 cm⁻¹ and

region below 275 cm⁻¹. As it can be seen from Figure 2, the W⁶⁺ ions have tetrahedral coordination. The free $[WO_4]^{2-}$ ion have T_d symmetry, and, when it placed into the scheelite structure, its point symmetry reduces to S_4 . The correlation between the free $[WO_4]^{2-}$ ion, site symmetry and factor grout symmetry of unit cell is given in Table S5. The high frequency part of spectrum (above 700 cm⁻¹) related to the stretching vibrations of $[WO_4]^{2-}$ ions. The strongest band at 915 cm⁻¹ is a v_1 symmetric stretching vibration of tungstate tetrahedron and the lines at 769 and 806 cm⁻¹ are v_3 antisymmetric stretching²⁵. Both bands at 327 and 375 cm^{-1} consists of couple of spectral lines and related to v_2 and v_4 bending vibration of $[WO_4]^{2-1}$ ions correspondingly^{25,26}. The spectral bands around 200 cm⁻¹ are the free rotational modes of $[WO_4]^{2-}$ ions^{27,28}. The experimental spectrum contain an extra band at 885 cm⁻¹. The appearance of extra lines in the region of $[WO_4]^{2-}$ vibrations can be explained as the local distortions of WO₄ tetrahedra caused by the influence of Na/Pb/La/Ho/Yb ions. The Raman spectra obtained from NPLW in comparison with NPLW doped with Yb³⁺ and Ho³⁺ are shown in Figure 7. The spectral bands below 425 cm⁻¹ can be interpreted as Raman-active vibrations, however, the region of stretching vibrations is covered with Ho³⁺ luminescence and only strong intensity line related to WO₄ symmetric stretching vibration is visible.

It is of interest to estimate the possibilities to control the spectral distribution in the UC luminescence by the chemical content of the host. Comparison of UC spectra of NaSrLa(WO₄)₃:Ho³⁺/Yb³⁺ [] and NaPbLa(WO₄)₃:Yb³⁺/Ho³⁺ (present work). Intensities of UC luminescent transitions at ${}^{5}S_{2}/{}^{5}F_{4} \rightarrow {}^{5}I_{8}$ and ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ channels are almost equal in the latter case, while in calcium-based crystal the latter channel prevails. In view of two-step process, the excitation of ${}^{5}F_{5}$ state is due to relaxation from upper states that are directly excited by UC energy transfer. Vibrational cutoff frequencies are close to each other in both hosts and are weakly influenced by heavy doping by rare earth ions. Therefore, the above mentioned effect must be ascribed to the crystal field engineering influence, namely, to the modification of wave functions of rare earth ions (either in in configurational space or via variation of Judd-Ofelt intensity parameters), that happens in case of change from calcium to lead and controls either non-radiative or radiative relaxation to ${}^{5}F_{5}$ state.

4. Conclusions

MAS based yellowish green phosphors of NaPbLa(WO₄)₃:Yb³⁺/Ho³⁺ new triple tungstates were successfully fabricated under variations of $x = Yb^{3+}/Ho^{3+}$ (x = 7, 8, 9, 10), showing the homogeneous crystallizations with particle size of 2-5 µm. Under excitation derived from 980 nm, the consequent phosphors brought to the formation of yellowish green emissions with the intense transitions of Ho³⁺ from the ${}^{5}S_{2}/{}^{5}F_{4} \rightarrow {}^{5}I_{8}$ in the green emission area, as well as the strong transitions from the ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ in the red emission area. The optimal ratio of Yb³⁺:Ho³⁺ was revealed to be 9:1. The chromaticity coordinates in CIE diagram corresponded to the yellowish green emissions. The strongly dominant Raman spectra were attributed to the concentration quenching effect of Ho³⁺ ions and to the superimposition by intense Ho³⁺ luminescence lines showing drastically longer wavelengths.

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Captions

Table 1. Abbreviation of the sample notations for NaPbLa(WO₄)₃:Yb³⁺/Ho³⁺ and ratio of Yb³⁺/Ho³⁺ = 7, 8, 9, 10.

Fig. 1. The difference Rietveld plot of NPLW.

Fig. 2. The crystal structure of NPLW. The unit cell is outlined. The lone atoms are omitted for clarity.

Fig. 3. SEM images of synthesized (a) NPLW, (b) NPLW:Yb0.35Ho0.05, (c) NPLW:Yb0.40Ho0.05, (d) NPLW:Yb0.45Ho0.05, and (e) NPLW:Yb0.50Ho0.05 particles.

Fig. 4. The UC photoluminescence emission spectra of (a) NPLW:Yb0.35Ho0.05, (b) NPLW:Yb0.40Ho0.05, (c) NPLW:Yb0.45Ho0.05 and (d) NPLW:Yb0.50Ho0.05 particles excited by 980 nm at room temperature.

Fig. 5. Logarithmic scale dependence of the upconversion emission intensity on the pump power in the range of 20 to 110 mW at 545 and 655 nm in the NPLW:Yb0.45Ho0.05 sample.

Fig. 6. CIE chromaticity diagram showing the color co-ordinates of the NPLW:YbHo phosphors. The inset shows the yellow emissions for the synthesized samples: (a) NPLW:Yb0.35Ho0.05, (b) NPLW:Yb0.40Ho0.05, (c) NPLW:Yb0.45Ho0.05, and (d) NPLW:Yb0.50Ho0.05 particles.

Fig. 7. Raman spectra of NPLW and NPLW:Yb³⁺,Ho³⁺ samples.

Table 1

Abbreviation of the samples	Ratio of Yb ³⁺ /Ho ³⁺	NaPbLa(WO ₄) ₃ :Yb ³⁺ /Ho ³⁺
NPLW		NaPbLa(WO4)3
NPLW:Yb0.35Ho0.05	7	NaPbLa _{0.6} (WO ₄) ₃ :Yb ³⁺ _{0.35} /Ho ³⁺ _{0.05}
NPLW:Yb0.40Ho0.05	8	NaPbLa _{0.55} (WO ₄) ₃ :Yb ³⁺ _{0.40} /Ho ³⁺ _{0.05}
NPLW:Yb0.45Ho0.05	9	NaPbLa _{0.50} (WO ₄) ₃ :Yb ³⁺ _{0.45} /Ho ³⁺ _{0.05}
NPLW:Yb0.50Ho0.05	10	NaPbLa _{0.45} (WO ₄) ₃ :Yb ^{3+0.50} /Ho ^{3+0.05}



Fig. 1.



Fig. 2.



Fig. 3.



Fig. 2



Fig. 4.









Fig. 6.



Supporting Information

Fabrication of Microcrystalline NaPbLa(WO₄)₃:Yb³⁺/Ho³⁺ Phosphors and Their Upconversion Photoluminescent Characteristics

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Compound	K N	Sp Gr	7	Cell parameters (Å),	$R_p, R_B(\%)$
Compound	х, у	sp.01.	L	Cell volume (Å ³)	χ^2
				<i>a</i> = 5.3927 (1)	22 40 8 02
NPLW	0, 0	$I4_{1}/a$	4	<i>c</i> = 11.7961 (3)	22.40, 0.92
				V = 343.05 (2)	1.57
NDL W.				a = 5.3507(2)	1670 262
$\mathbf{NPLW}:$	0.05, 0.35	$I4_{1}/a$	4	c = 11.6978 (4)	10.70, 2.02
0.05H0,0.35YD				V = 334.90 (3)	1.37
NDL W.				a = 5.3384(2)	12 49 1 77
NPLW:	0.05, 0.4	$I4_{1}/a$	4	c = 11.6704 (4)	13.48, 1.77
0.05H0,0.4 Y D				V = 332.59 (2)	1.22
NDL W.				a = 5.3373(2)	14.26.2.26
NPLW:	0.05, 0.45	$I4_{1}/a$	4	c = 11.6651 (4)	14.30, 3.30
0.05H0,0.45YD		V = 332.31 (2)	1.30		
NDL W.				a = 5.3331(2)	12.07 1.61
NPLW:	0.05, 0.5	$I4_{1}/a$	4	c = 11.6585 (6)	13.87, 1.01
0.05H0,0.5YD	0.0310,0.310		<i>V</i> = 331.59 (3)	1.29	

Table S1. Main parameters of processing and refinement of the NaPbLa_{1-x-y}WO₄:*x*Ho,*y*Yb samples

	X	у	Z	$B_{ m iso}$	Occ.	
NPLW						
Na	0	1/4	5/8	0.2 (2)	1/3	
Pb	0	1/4	5/8	0.2 (2)	1/3	
La	0	1/4	5/8	0.2 (2)	1/3	
W	0	1/4	1/8	0.5 (2)	1	
0	0.206 (6)	0.089 (5)	0.0396 (15)	0.5 (7)	1	
		NPLW:0.	05Ho,0.35Yb			
Na	0	1/4	5/8	0.84 (18)	1/3	
Pb	0	1/4	5/8	0.84 (18)	1/3	
La	0	1/4	5/8	0.84 (18)	0.2	
Но	0	1/4	5/8	0.84 (18)	0.01666667	
Yb	0	1/4	5/8	0.84 (18)	0.1166667	
W	0	1/4	1/8	0.63 (18)	1	
0	0.237 (4)	0.090 (3)	0.0457 (9)	3.0 (6)	1	
	NPLW:0.05Ho,0.4Yb					
Na	0	1/4	5/8	1.52 (14)	1/3	
Pb	0	1/4	5/8	1.52 (14)	1/3	
La	0	1/4	5/8	1.52 (14)	0.1833333	
Er	0	1/4	5/8	1.52 (14)	0.01666667	
Yb	0	1/4	5/8	1.52 (14)	0.1333333	
Mo	0	1/4	1/8	1.64 (14)	1	
0	0.235 (3)	0.1035 (19)	0.0445 (8)	2.5 (4)	1	
NPLW:0.05Ho,0.45Yb						
Na	0	1/4	5/8	1.11 (17)	1/3	
Pb	0	1/4	5/8	1.11 (17)	1/3	
La	0	1/4	5/8	1.11 (17)	0.1666667	
Er	0	1/4	5/8	1.11 (17)	0.01666667	
Yb	0	1/4	5/8	1.11 (17)	0.15	

Table S2. Fractional atomic coordinates and isotropic displacement parameters (Å²) of the NaPbLa_{1-x-y}MoO₄:*x*Er,*y*Yb samples

Mo	0	1/4	1/8	1.07 (17)	1
0	0.242 (3)	0.091 (2)	0.0496 (8)	1.9 (4)	1
		NPLW:().05Ho,0.5Yb		
Na	0	1/4	5/8	1.3 (2)	1/3
Pb	0	1/4	5/8	1.3 (2)	1/3
La	0	1/4	5/8	1.3 (2)	0.15
Er	0	1/4	5/8	1.3 (2)	0.01666667
Yb	0	1/4	5/8	1.3 (2)	0.1666667
Mo	0	1/4	1/8	1.6 (2)	1
0	0.221 (5)	0.091 (4)	0.0467 (13)	2.3 (6)	1

Table S3. Main bond lengths (Å) of the NaPbLa_{1-x-y}WO₄:xHo,yYb samples

NPLM				
(Na/Pb/La)—O ⁱ	2.62 (3)	W—O	1.77 (2)	
(Na/Pb/La)—O ⁱⁱ	2.66 (2)			
	NPLW:0.05Ho	o,0.35Yb		
(Na/Pb/La/Ho/Yb)—O ⁱ	2.481 (16)	W—O	1.789 (16)	
(Na/Pb/La/Ho/Yb)—O ⁱⁱ	2.588 (16)			
	NPLW:0.05H	o,0.4Yb		
(Na/Pb/La/Ho/Yb)—O ⁱ	2.540 (14)	W—O	1.750 (14)	
(Na/Pb/La/Ho/Yb)—O ⁱⁱ	2.560 (11)			
	NPLW:0.05Ho	o,0.45Yb		
(Na/Pb/La/Ho/Yb)—O ⁱ	2.443 (15)	W—O	1.781 (15)	
(Na/Pb/La/Ho/Yb)—O ⁱⁱ	2.601 (11)			
	NPLW:0.05H	o,0.5Yb		
(Na/Pb/La/Ho/Yb)—O ⁱ	2.52 (2)	W—O	1.72 (2)	
(Na/Pb/La/Ho/Yb)—O ⁱⁱ	2.634 (17)			

Symmetry codes: (i) -x+1/2, -y, z+1/2; (ii) -x+1/2, -y+1/2, -z+1/2.



Figure S1. Difference Rietveld plot of NPLM: 0.35Yb,0.05Ho.



Figure S2. Difference Rietveld plot of NPLM: 0.40Yb,0.05Ho.



Figure S3. Difference Rietveld plot of NPLM: 0.45Yb,0.05Ho.



Figure S4. Difference Rietveld plot of NPLM: 0.50Yb,0.05Ho.



Figure S5. The dependence of cell volume on averaged ion radii IR(Na/Pb/La/Ho/Yb) of NPLW: xHo^{3+} , yYb^{3+} .



Figure S6. The dependence of cell volume on averaged ion radii IR(Na/Pb/La/Ho/Yb) of NPLW: xHo³⁺,yYb³⁺ among other representative scheelite-type tungstates.



Figure S7. Raman spectra of NPLW powder.

Compound	V, Å ³	Reference
BaWO ₄	399.46	[1]
$Ba_{0.75}Sr_{0.25}WO_4$	386.01	[1]
$Ba_{0.5}Sr_{0.5}WO_4$	373.15	[1]
$Ba_{0.25}Sr_{0.75}WO_4$	358.46	[1]
$K_{0.5}La_{0.5}WO_4$	358.41	[2]
PbWO ₄	357.25	[3]
$Pb_{0.5}Sr_{0.5}WO_4$	355.02	[4]
$SrWO_4$	352.48	[1]
$EuWO_4$	350.31	[5]
$Sr_{0.75}Ca_{0.225}WO_4$	342.78	[1]
$Na_{1/3}Sr_{1/3}La_{1/3}WO_4$	340.02	[6]
$Na_{1/3}Pb_{1/3}La_{1/3}WO_4$	343.05(2)	Current work
Na1/3Pb1/3La1/3WO4: 0.05Ho,0.35Yb	334.90(3)	Current work
Na _{1/3} Pb _{1/3} La _{1/3} WO ₄ : 0.05Ho,0.4Yb	332.59(2)	Current work
Na _{1/3} Pb _{1/3} La _{1/3} WO ₄ : 0.05Ho,0.45Yb	332.31(2)	Current work
$Na_{1/3}Pb_{1/3}La_{1/3}WO_4$: 0.05Ho,0.5Yb	331.59(3)	Current work
$Sr_{0.5}Ca_{0.5}WO_4$	332.14	[1]
$Sr_{0.25}Ca_{0.75}WO_4$	323.15	[1]
Na _{0.5} Bi _{0.5} WO ₄	320.96	[7]
Na0.55Eu0.45WO4	315.1	[8]
$Na_{0.5}Dy_{0.5}WO_4$	314.83	[9]
$CaWO_4$	312.72	[10]
$Na_{0.5}Gd_{0.5}WO_4$	309.74	[11]
$Na_{0.47}Gd_{0.53}WO_4$	309.21	[12]
$Na_{0.24}Gd_{0.59}Yb_{0.17}WO_{4}$	309.34	[11]
$Ca_{0.5}Cd_{0.5}WO_4$	305.2	[13]
$Na_{0.5}Y_{0.5}WO_4$	304.81	[14]
$Li_{0.5}La_{0.5}WO_4$	328.92	[15]
$Li_{0.5}Nd_{0.5}WO_4$	315.59	[15]
$Li_{0.5}Sm_{0.5}WO_4$	309.19	[15]

Table 4S. Known scheelite-type tungstates and their cell volumes

$Li_{0.5}Eu_{0.5}WO_4$	306.65	[15]
$Li_{0.5}Gd_{0.5}WO_4$	304.19	[15]
$Li_{0.5}Tb_{0.5}WO_4$	301.7	[15]

Table S5. Correlation diagram between T_d point symmetry, S_4 sites symmetry and C_{4h} factor group symmetry for WO₄ tetrahedra

Wavenumber, cm ⁻¹	T_d	S_4	C_{4h}
[16]	Point group	Site symmetry	Factor group
			symmetry
897	$A_{1}(v_{1})$	A	A_g+B_u
317	$E(v_2)$	$A{+}B$	$A_g + B_u + Bg + Au$
837	$F_2(v_3)$	$B + \{{}^{2}E, {}^{1}E\}$	$B_g + A_u + E_g + E_u$
-	$F_2(v_4)$	$B + \{{}^{2}E, {}^{1}E\}$	$B_g + A_u + E_g + E_u$

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