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Registry No. Eu_3TaO_7 , 12444-76-7; Eu_3TaO_6 , 55763-53-6; $\text{Eu}_3\text{TaO}_{5.5}$, 61075-76-1; $\text{Eu}(\text{Lu}_{0.5}\text{Ta}_{0.5})\text{O}_3$, 60923-91-3; EuTaO_3 , 61075-74-9; $\text{Eu}_4\text{Ta}_2\text{O}_9$, 61075-75-0; Eu_2O_3 , 1308-96-9; Ta_2O_5 ,

1314-61-0; Ta, 7440-25-7; EuO , 12020-60-9.

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Preparation and Properties of the Scheelite-Type $\text{LnGe}_{0.5}\text{W}_{0.5}\text{O}_4$ Compounds

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The title compositions were prepared for all rare earth ions (except Pm) as well as for Ln being Y, La, and Bi. The Sc compound did not form and the Ga composition exhibits another structure. All materials studied (except Ga) crystallize in an undistorted, disordered scheelite structure, space group $I4_1/a$. The lattice parameters and excitation and emission spectra of the fluorescing compositions are reported.

Introduction

Compounds of the type $\text{LnGe}_{0.5}\text{W}_{0.5}\text{O}_4$ can be looked upon as IV–VI substitutions for pentavalent Nb^{5+} in the LnNbO_4 rare earth niobates. This type of substitution with Ti^{4+} in the unusual tetrahedral coordination was first described in 1964.¹ These $\text{LnM}_{0.5}\text{Ti}_{0.5}\text{O}_4$ compounds (where M can be either Mo^{6+} or W^{6+}) crystallize almost exclusively in the scheelite (CaWO_4) rather than in the fergusonite (YNbO_4) structure. Blasse² later also prepared some of these titanates as well as some of the equivalent germanates with Ln being La, Gd, Y, and Lu. $\text{LnGe}_{0.5}\text{Mo}_{0.5}\text{O}_4$ compounds with Ln being Pr, Nd, Gd, Tb, Dy, Ho, Er, and Yb were described by Finch et al.³

The present paper reports the preparation of all $\text{LnGe}_{0.5}\text{W}_{0.5}\text{O}_4$ rare earth compounds as well as the Ga, Y, La, and Bi compositions. The fluorescent behavior of the active ions Sm^{3+} , Eu^{3+} , Tb^{3+} , Dy^{3+} , and Tm^{3+} in $\text{LnGe}_{0.5}\text{W}_{0.5}\text{O}_4$ as a host is also described.

Experimental Section

All compounds were prepared by the standard solid-state technique of prefiring the stoichiometric constituent oxide components (GeO_2 , electronic grade from Eagle Pitcher; WO_3 , purified analytical grade from Fisher Scientific Co.; and Ln_2O_3 , 99.99% from Research Co. Chemicals) at 1000 °C for 10–14 h, ball-milling and refiring at 1100 and 1200 °C for 4 h each. A single crystal of $\text{LaGe}_{0.5}\text{W}_{0.5}\text{O}_4$ was grown by the Czochralski technique from an Ir crucible in air. The melting point of this composition is 1526 °C, and excessive vaporization (GeO_2) occurred even at 150 psi. Since all other rare earth compounds would melt even higher, no attempts were made to grow those crystals.

The x-ray parameters were obtained by a least-squares treatment of d values read from Guinier-Hagg films. Fluorescence data were measured with a Perkin Elmer Model MPF-2A spectrophotometer.

Results and Discussion

A. Structure. Table I summarizes the lattice parameters, cell volumes, and calculated x-ray densities of the studied compounds. The cell edges marked with asterisks are those previously reported by Blasse² and are in good agreement. As one can see, all of the rare earth compounds, including Y and

Table I. Lattice Parameters and Densities of the $\text{LnW}_{0.5}\text{Ge}_{0.5}\text{O}_4$ Compounds^a

Compn	a_0 , Å	c_0 , Å	ρ , g ml ⁻¹
$\text{YW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.089	11.089	6.50 ₂
$\text{LaW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.266	11.813	6.71 ₃
$\text{CeW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.220	11.620	6.97 ₁
$\text{PrW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.219	11.572	7.01 ₇
$\text{NdW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.203	11.486	7.25 ₅
$\text{SmW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.170	11.356	7.49 ₅
$\text{EuW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.152	11.307	7.61 ₈
$\text{GdW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.141	11.257	7.80 ₆
$\text{TbW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.122	11.195	7.94 ₁
$\text{DyW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.107	11.149	8.10 ₂
$\text{HoW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.094	11.098	8.23 ₆
$\text{ErW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.079	11.098	8.39 ₀
$\text{TmW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.061	10.998	8.51 ₄
$\text{YbW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.045	10.956	8.69 ₇
$\text{LuW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.035	10.926	8.80 ₅
$\text{BiW}_{0.5}\text{Ge}_{0.5}\text{O}_4$	5.215	11.596	8.44 ₇

^a $\text{GaW}_{0.5}\text{Ge}_{0.5}\text{O}_4$ crystallized in orthorhombic symmetry with $a = 9.503$ Å, $b = 9.634$ Å, and $c = 13.352$ Å.

La, do crystallize in the same structure. This is in contrast to the three different structural types occurring, for instance, in the $\text{Ln}_2(\text{MoO}_4)_3$ molybdates.⁴ Other rare earth series, such as the niobates,⁵ also exhibit only one structural prototype. As mentioned earlier, the Ga composition crystallizes in different, orthorhombic symmetry, space group $Pbcn$ (D_{2h}^{14}), point group mmm . Since according to Shannon⁶ Ga^{3+} in octahedral coordination has a radius of 0.62 Å and the smallest rare earth (Lu) has one of 0.86 Å, the size limitation for the stability of the scheelite structure for the $\text{LnGe}_{0.5}\text{W}_{0.5}\text{O}_4$ type must be somewhere between these two numbers. The fact that $\text{LuGe}_{0.5}\text{W}_{0.5}\text{O}_4$ still does form a scheelite is surprising, since in the case of the pure tungstates Cd^{2+} (0.95 Å) in CdWO_4 already crystallizes in the different wolframite ($P2_1/a$) structure.

If one plots the cube of Shannon's⁶ radii vs. the cell volume, an excellent straight-line relationship is obtained as seen in

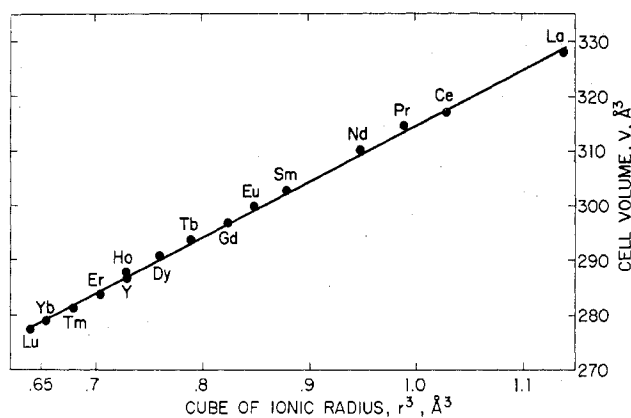


Figure 1. Cube of ionic radius, r^3 vs. cell volume for the $\text{LnGe}_{0.5}\text{W}_{0.5}\text{O}_4$ compounds.

Table II. Observed and Calculated d Values for $\text{LaGe}_{0.5}\text{W}_{0.5}\text{O}_4^a$

Intens	h	k	l	d , Å	
				Obsd	Calcd
10	1	0	1	4.7921	4.7991
75	0	0	4	2.9489	2.9476
100	2	0	0	2.6276	2.6270
5	2	0	2	2.4000	2.3995
30	1	1	4	2.3075	2.3091
10	1	0	5	2.1520	2.1513
10	2	1	3	2.0165	2.0167
95	2	0	4	1.9621	1.9611
70	2	2	0	1.8580	1.8575
80	1	1	6	1.7373	1.7370
95	3	1	2	1.5990	1.5991
10	0	0	8	1.4737	1.4738
5	3	1	4	1.4469	1.4473
25	4	0	0	1.3131	1.3135
60	3	1	6	1.2686	1.2687
30	3	3	2	1.2119	1.2119
20	4	0	4	1.1999	1.1997
30	4	2	0	1.1749	1.1748
20	2	2	8	1.1545	1.1545
20	1	1	10	1.1237	1.1238

^a $a = 5.266$ (1) Å, $c = 11.813$ (2) Å, $V = 327.6$ (1) Å³, and space group is $I4_1/a$.

Table III. Observed and Calculated d Values of $\text{GaGe}_{0.5}\text{W}_{0.5}\text{O}_4^a$

Intens	h	k	l	d , Å	
				Obsd	Calcd
15	0	0	2	6.6608	6.6761
35	1	1	1	6.0249	6.0347
30	0	2	0	4.8040	4.8160
25	1	1	2	4.7503	4.7519
35	0	2	1	4.5270	4.5303
50	2	1	0	4.2604	4.2615
55	1	2	1	4.0857	4.0894
60	2	1	1	4.0529	4.0598
75	1	0	3	4.0315	4.0306
10	0	2	2	3.9074	3.9058
5	2	0	2	3.8720	3.8714
35	1	1	3	3.7205	3.7182
55	1	2	2	3.6123	3.6126
50	2	2	0	3.3827	3.3825
30	0	0	4	3.3383	3.3380
75	0	2	3	3.2659	3.2686
100	2	0	3	3.2434	3.2484

^a $a = 9.503$ (3) Å, $b = 9.634$ (2) Å, $c = 13.352$ (4) Å, $V = 1222.4$ Å³, and space group is $Pbcn$ (D_{2h}^{14}).

Figure 1, suggesting that even for the smaller rare earths there is no tendency toward a change of coordination. A comment should be made about $\text{BiGe}_{0.5}\text{W}_{0.5}\text{O}_4$. If the determined cell volume is plotted in Figure 1, the extrapolated radius for Bi^{3+}

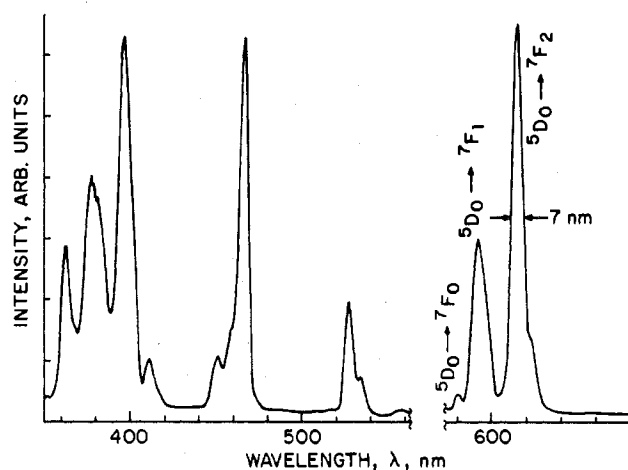


Figure 2. Excitation (left) and emission (right) spectra of $\text{EuGe}_{0.5}\text{W}_{0.5}\text{O}_4$.

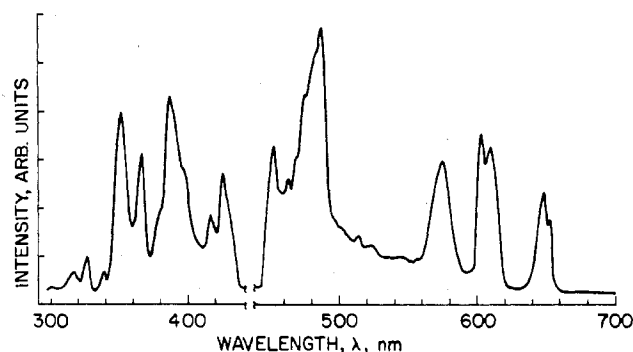


Figure 3. Excitation (left) and emission (right) spectra of $\text{Sm}_{0.1}\text{La}_{0.9}\text{Ge}_{0.5}\text{W}_{0.5}\text{O}_4$.

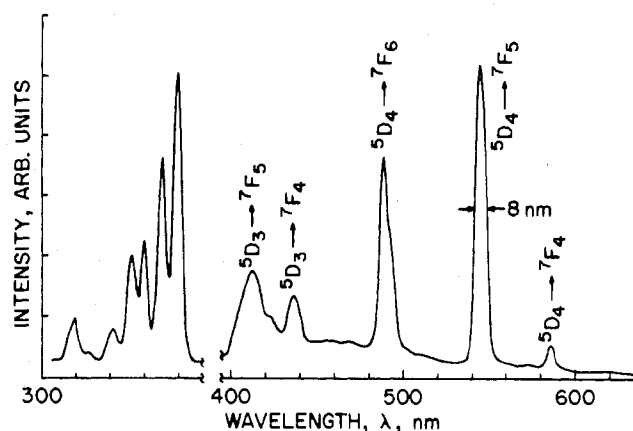


Figure 4. Excitation (left) and emission (right) spectra of $\text{Tb}_{0.1}\text{La}_{0.9}\text{Ge}_{0.5}\text{W}_{0.5}\text{O}_4$.

would be 1.00 Å, or 0.03 Å smaller than Shannon's⁶ value. This is, however, completely consistent with the fact that the Bi^{3+} radius is reduced to about 95% of the size of La^{3+} once the Bi ion is constrained into highly symmetric sites such as we have in the scheelite.⁷ As soon as the lone electron pair of the Bi^{3+} ion comes into play and Bi usually occupies asymmetric sites, its radius is closer to La^{3+} . Table II gives the observed and calculated d values for $\text{LaGe}_{0.5}\text{W}_{0.5}\text{O}_4$ and Table III reports the first 20 d values for the orthorhombic $\text{GaGe}_{0.5}\text{W}_{0.5}\text{O}_4$.

B. Fluorescence. Of all $\text{LnGe}_{0.5}\text{W}_{0.5}\text{O}_4$ compounds with 100% occupancy of any single rare earth ion in the cation sites, only $\text{EuGe}_{0.5}\text{W}_{0.5}\text{O}_4$ fluoresced intensely under 3660-Å, 2537-Å, UV, or electron excitation, indicating that in this case no concentration quenching of the Eu^{3+} emission occurs. The

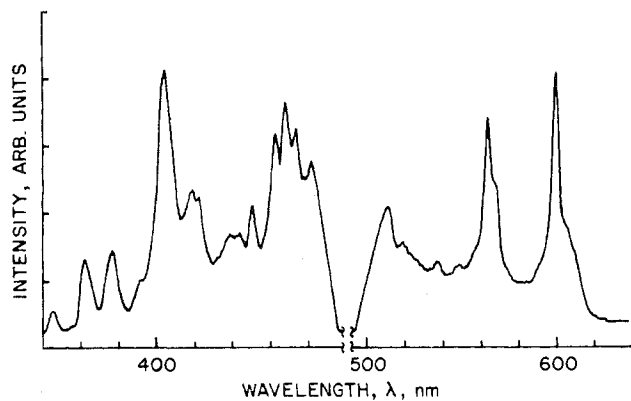


Figure 5. Excitation (left) and emission (right) spectra of $\text{Dy}_{0.1}\text{La}_{0.9}\text{Ge}_{0.5}\text{W}_{0.5}\text{O}_4$.

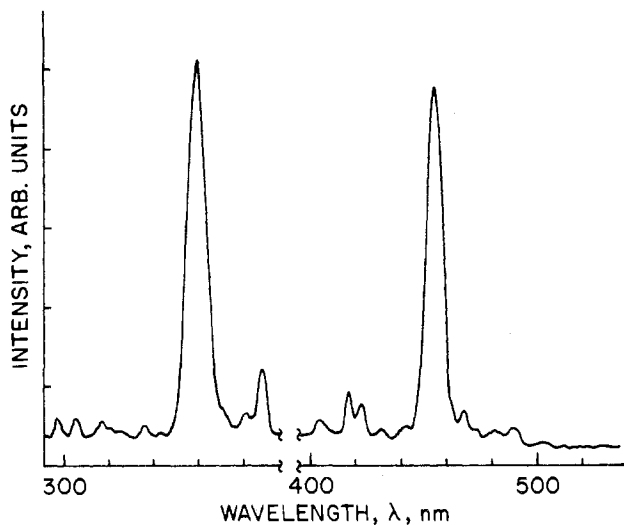


Figure 6. Excitation (left) and emission (right) spectra of $\text{Tm}_{0.1}\text{La}_{0.9}\text{Ge}_{0.5}\text{W}_{0.5}\text{O}_4$.

emission and excitation spectra are shown in Figure 2. Greater than 95% of the total emission stems from the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and the electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions, while the balance of the luminescence arises from the normally forbidden ($J = 0 \rightarrow J = 0$) $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition, clearly visible at 580 nm in Figure 2. Blasse² made a point of the fact that the Eu^{3+} emission lines are relatively broad due to the variation of crystal field caused by the disordered array of Ge and W ions around the Eu^{3+} site. While we fully agree with the experimental fact (see half-width of the 616-Å line of 7.0 nm in Figure 1), we cannot concur with the conclusion that this

supports the existence of a disordered structure, since Eu^{3+} in EuNbO_4 yielded virtually the identical spectrum with a half-width of the same 616-Å line of only 0.2 nm less. As stated before, the Eu compound was the only one to fluoresce in the pure state. We therefore incorporated all other luminescing ions (Sm, Tb, Dy, and Tm) at the 0.1-mol level in $\text{LaGe}_{0.5}\text{W}_{0.5}\text{O}_4$. The $\text{Sm}_{0.1}\text{La}_{0.9}\text{Ge}_{0.5}\text{W}_{0.5}\text{O}_4$ spectra are shown in Figure 3. Figure 4 gives the Tb^{3+} spectra, and this example also warrants some comment, as Blasse² stated Tb^{3+} does not fluoresce in the $\text{LnGe}_{0.5}\text{W}_{0.5}\text{O}_4$ host. The compound $\text{Tb}_{0.1}\text{La}_{0.9}\text{Ge}_{0.5}\text{W}_{0.5}\text{O}_4$ fluoresces quite intensely, as can be seen in Figure 4. The green $^5\text{D}_4 \rightarrow ^7\text{F}$ transitions are clearly dominant over the blue $^5\text{D}_3 \rightarrow ^7\text{F}$ transitions. Diffuse reflectance measurements on the pure host $\text{LaGe}_{0.5}\text{W}_{0.5}\text{O}_4$ yielded a band edge of 287 nm, which will readily allow this type of emission. This absorption edge is intermediate to the two types of tungstate hosts, Y_2WO_6 (300 nm) and $\text{Y}_2(\text{WO}_4)_3$ (245 nm), previously studied for Tb^{3+} activation by Blasse.⁸ Only the latter was found to support Tb^{3+} emission.

Luminescence was also observed for Dy^{3+} and Tm^{3+} in the $\text{LaGe}_{0.5}\text{W}_{0.5}\text{O}_4$ host and their spectra are shown in Figures 5 and 6.

In summary we can state that $\text{LaGe}_{0.5}\text{W}_{0.5}\text{O}_4$ is an interesting scheelite structure host which allows the study of rare earth fluorescence without the further complication of valence compensation either in the cation⁸ or anion sites.⁹

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Registry No. $\text{YW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 12362-39-9; $\text{LaW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 12362-37-7; $\text{CeW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 60967-30-8; $\text{PrW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 60967-35-3; $\text{NdW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 60967-34-2; $\text{SmW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 60967-36-4; $\text{EuW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 60967-32-0; $\text{GdW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 53851-55-1; $\text{TbW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 53851-57-3; $\text{DyW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 53851-45-9; $\text{HoW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 53851-56-2; $\text{ErW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 53851-47-1; $\text{TmW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 60967-37-5; $\text{YbW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 60967-38-6; $\text{LuW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 12362-38-8; $\text{BiW}_{0.5}\text{Ge}_{0.5}\text{O}_4$, 60967-28-4; $\text{GaGe}_{0.5}\text{W}_{0.5}\text{O}_4$, 60967-33-1.

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