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Luminescence and X-ray Studies of the $LuTa_{1-x}Nb_xO_4$ System

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Rare earth tantalates occur in at least four different compositions, ranging from a 1:7 Ln:Ta ratio in $LnTa_7O_{19}$ ($P6_3/mcm$) to a Ln:Ta ratio of 3:1 in Ln_3TaO_7 ($Fm3m$), with $LnTa_5O_{14}$ ($Pna2_1$) and $LnTaO_4$ ($I1/a$ or $P2/a$) being intermediate to those compositions (Ln = lanthanide) [1, 2]. The latter composition actually exists in four structural modifications: the $P2_1/n$ structure for Ln = La, Ce and Pr [3], the $I2/a$ M (or fergusonite) structure for Ln = Nd to Lu [4], the $P2/a$ M′ structure for Ln = Sm to Lu [2] and finally the tetragonal $I4_1/a$ scheelite structure to which all compounds convert at high temperature [5]. As far as luminescence is concerned, only the M′ modification of $LnTaO_4$ constitutes an efficient host under X-ray excitation. First reports on the fluorescence of some tantalates were given in 1964 by Brixner [6], and later Blasse and Bril [7] studied the fergusonite-type hosts $GdTaO_4$, $YTaO_4$ and $LuTaO_4$ with a variety of activators, primarily under UV excitation. M′-$YTaO_4$ (Nb or Tm doped) proved to be an efficient phosphor under X-ray excitation and two commercial X-ray intensifying screens (Quanta Detail, $Y_{0.998}Tm_{0.002}TaO_4$ and Quanta Fast Detail, $YTa_{0.98}Nb_{0.02}O_4$) have been developed by Du Pont. In fact, together with green emitting Gd_2O_2S:Tb [8] and blue emitting LaOBr:Tm [9] these are the only three modern phosphors used in X-ray intensifying screens. It is the purpose of the present paper to examine M′-$LuTaO_4$ in detail as a potential phosphor for X-ray intensifying screens. In applications calling for very thin (and also very sharp) screens the considerable cost of the raw materials would be largely compensated by the outstanding density (9.81 g cm^{-3}) and superb X-ray absorption of $LuTaO_4$.

Experimental

Phosphor Preparation

The raw materials used for the phosphor preparation were of the highest commercial purity: Ta_2O_5 and Nb_2O_5 were Cabot's 'optical grade' and Lu_2O_3 was of nominal 99.9% purity from Research Chemicals. The constituent stoichiometric components were blended via Sweco milling in a urethane lined vessel, using Al_2O_3 pebbles as milling medium and Freon® TF as fluid. After filtering and drying, this blend was mixed with half its weight of Li_2SO_4 and firing was carried out in recrystallized Al_2O_3 containers at 1250 °C for periods from 10 to 16 h. After cooling the flux was leached with water, the phosphor was filtered on a frit, washed with water and methanol and dried at 120 °C. Yields were generally 95 to 98% of theory. Phosphor prepared this way was generally polyhedral with only slight elongation along one axis. Particle size was typically in the 3–6 μ range with surface areas of 0.15 to 0.20 m^2/g. A typical SEM of M′-$LuTa_{0.99}Nb_{0.01}O_4$ is shown in Fig. 1.

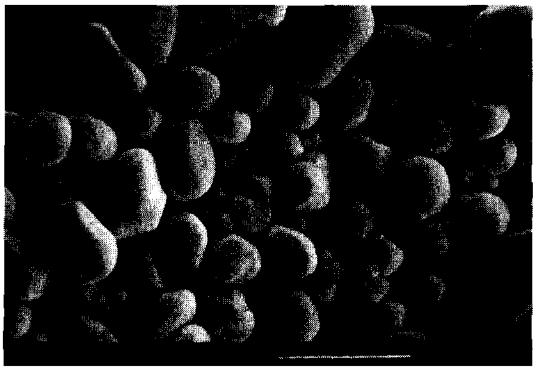

Fig. 1. SEM of M′-$LuTa_{0.99}Nb_{0.01}O_4$ at 1800×.

X-ray Studies

The X-ray powder diffraction data were collected with a Philips APD3600-02 diffractometer, automated with a Data General Nova 4/X computer. The unit was equipped with a long, fine focus Cu tube, a theta-compensating slit, and a graphite diffracted-beam monochrometer. Samples were prepared by a thin smear method. The data was stripped of alpha-two peaks and peak positions were corrected with silicon as an internal standard. The corrected two-theta values were used in a least-squares refinement of the lattice parameters (local program).

Optical Studies

X-ray excited spectra were obtained in a set-up shown schematically in Fig. 2. The Siemens 710H generator equipped with a molybdenum tube was usually operated at 10 mA and 30 kVp. The monochrometer used was a Spex Fluorolog model.

Results and Discussion

Structural Data

As was previously pointed out for $YTaO_4$ [2], $LuTaO_4$ also crystallizes in two modifications: the M

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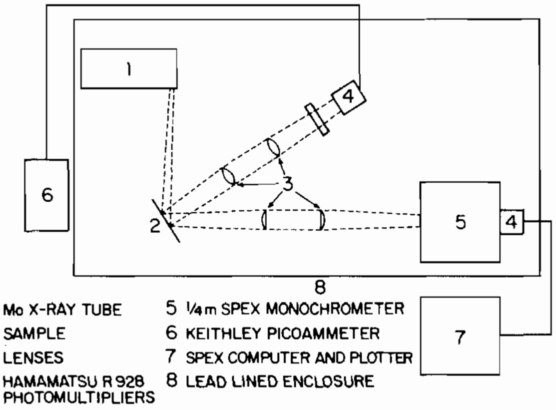

Fig. 2. Schematic of equipment used to study phosphors under X-ray excitation.

(or fergusonite) structure which is derived from the tetragonal high temperature scheelite structure via a reversible, second-order, purely ferroelastic phase transition $4/mF2/m$. The two domain walls required by Aizu [10] for this transformation have been observed. The M′ modification of LuTaO$_4$ is the smallest to exist for that structure. M-TaO4 tantalates with cations smaller than Lu^{3+}, such as ScTaO$_4$ and InTaO$_4$ [11] do crystallize in the different $P2/c$ wolframite structure and no solid solubility of those with M′-LuTaO$_4$ was observed. Cell parameters for the two LuTaO$_4$ structures are summarized in Table I.

M′-LuTaO$_4$ is the most stable of all existing M′-LnTaO$_4$ compositions (Sm to Lu) and in order to convert the M′ modification to the M structure it had to be heated to >1600 °C or pressure had to be applied at 1600 °C. This conversion is by way of a disruptive first-order phase transformation to scheelite and subsequent distortion to M by cooling. The M and M′ structures cannot directly be converted into each other. Since M′-LnTaO$_4$ is always obtained at the lower temperature, it constitutes the true room temperature equilibrium phase and the M modification exists in a metastable state. As we shall see in the following section on luminescence, partial Nb substitution for Ta strongly enhanced the luminescence in a manner similar to the M′-YTa$_{1-x}$Nb$_x$O$_4$ system [2]. Before studying these properties we had to examine the X-ray phase diagram of the LuTaO$_4$–LuNbO$_4$ system and these data are summarized in Table II.

TABLE II. Cell Dimensions for the LuTa$_{1-x}$Nb$_x$O$_4$ System

x	Type	a (Å)	b (Å)	c (Å)	deg	V (Å^3)
0	M′	5.238	5.427	5.062	96.1	143.08
0.01	M′	5.237	5.426	5.059	95.9	142.99
0.02	M′	5.238	5.421	5.058	95.9	142.86
0.03	M′	5.236	5.423	5.056	95.8	142.83
0.05	M′	5.234	5.419	5.051	95.6	142.57
0.1	M′	5.232	5.418	5.050	95.2	142.56
0.3	M′	5.232	5.411	5.048	94.9	142.63
0.35		Two phase ~50% each M + M′				
0.4	M	5.232	10.824	5.049	94.8	284.92
0.6	M	5.231	10.825	5.044	94.5	284.74
0.8	M	5.230	10.821	5.043	94.6	284.48
0.9	M	5.228	10.821	5.042	94.4	284.44
1.0	M	5.229	10.822	5.043	94.3	284.57

If one compares the data in Table II with that for the YTa$_{1-x}$Nb$_x$O$_4$ system [2], it is obvious that the solid solubility of LuNbO$_4$ in the M′ modification of LuTaO$_4$ is twice as extensive up to $x = 0.3$, again followed by a two-phase region which becomes single-phase fergusonite type at $x = 0.4$. This phase relationship is also illustrated together with the luminescent data for the LuTa$_{1-x}$Nb$_x$O$_4$ system in Fig. 3.

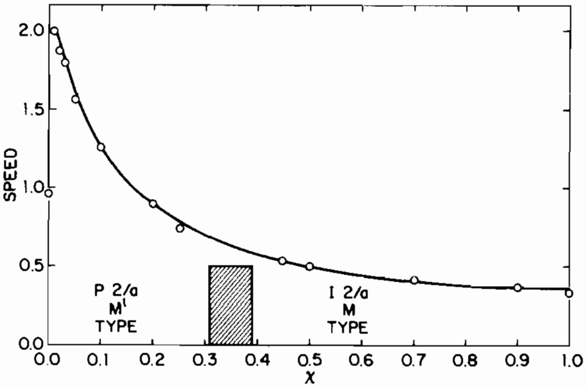

Fig. 3. X-ray phase diagram and speed for the LuTa$_{1-x}$Nb$_x$O$_4$ system.

Absorption Properties

The main reason for re-investigating LuTaO$_4$ (preliminary data were reported in refs. 2 and 6) is the fact that with a density of 9.8 g cm^{-3} and superb

TABLE I. Cell Parameters for M and M′-LuTaO$_4$

Modification	Space group	a (Å)	b (Å)	c (Å)	deg	V (Å)	$D_{\text{X-ray}}$ (g cm^{-3})
M	$I2/a$	5.253(1)	10.815(4)	5.024(2)	95.40(2)	142.11	9.81
M′	$P2/a$	5.238(2)	5.427(1)	5.062(1)	96.15(3)	143.08(2)	9.79

X-ray absorption in the medically important 10 to 80 kVp range it could be an outstanding phosphor for X-ray intensifying screens. Outside of ThO_2 (10.07 g cm^{-3}) and HfO_2 (10.30 g cm^{-3}), $LuTaO_4$ is the densest white material known. ThO_2 is of course radioactive and could therefore not be used in X-ray intensifying screens and efforts to utilize HfO_2 as an X-ray phosphor are described in ref. 12.

X-ray absorption as a function of energy relative to $CaWO_4$ and some other tantalates is shown in Fig. 4. In Fig. 5 we compare the absorption of 50 μ thin $LuTaO_4$ with Gd_2O_2S:Tb and $CaWO_4$ for the important low energy region, where Mo has its Kα (17.5 KeV) edge. It is quite obvious that for such applications, where the softer but more absorbing Mo radiation is used, $LuTaO_4$ is by far the best.

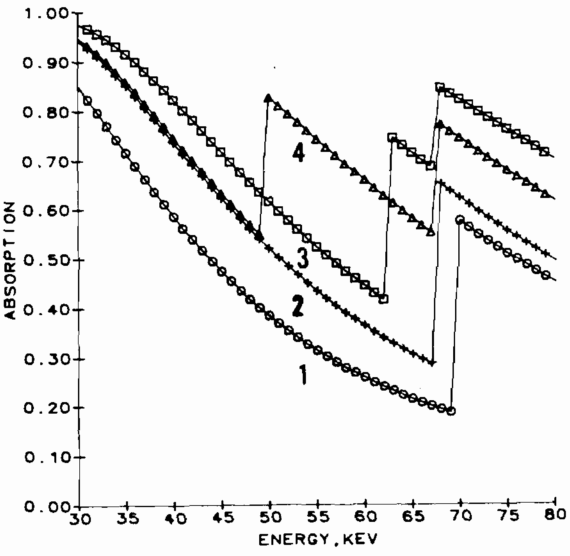

Fig. 4. X-ray absorption of 200 μ thick phosphors: $CaWO_4$ (1), $YTaO_4$ (2), $LuTaO_4$ (3) and $GdTaO_4$ (4).

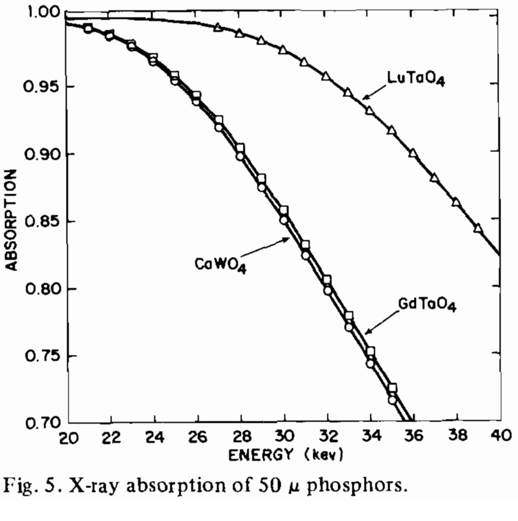

Fig. 5. X-ray absorption of 50 μ phosphors.

Luminescence

Preliminary luminescence data for $LuTa_{0.95}$-$Nb_{0.05}O_4$ under UV excitation were given in ref. 2 but no X-ray excited spectra were run. We have now completed the study by examining $LuTa_{1-x}Nb_xO_4$ under X-ray excitation. Pure $LuTaO_4$ can readily be X-ray excited and yields emission are shown in Fig. 6. This is very similar to $YTaO_4$ [2] in which Y^{3+} has no f electrons while Lu^{3+} has a completely filled shell with 14 electrons and therefore of course also no f → f transitions. Nb doping of $LuTaO_4$ greatly enhances the emission via energy transfer from the absorbing TaO_4 group to the emitting NbO_4 species. The emission also shifts to lower energy, as can be seen in Fig. 7. Figure 3 shows the dependence of the luminescent intensity as a function of the Nb concentration. This is similar to the $YTa_{1-x}Nb_xO_4$ system but the concentration dependence of the peak emission is even steeper in this case and occurs at $x = 0.01$.

Phosphor preparation for these materials was identical to that described in ref. 2 and a typical SEM of $LuTa_{0.99}Nb_{0.01}O_4$ is shown in Fig. 1. The surface areas of such powders generally were below 0.20 m^2/g. Commercial size (20 X 24 cm) screens

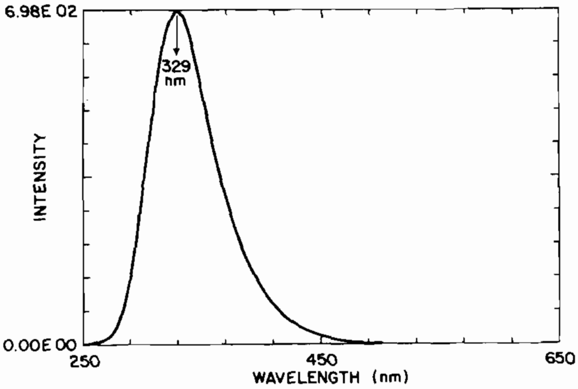

Fig. 6. 20 mA/40 kVp (Mo) X-ray excited emission spectrum of $LuTaO_4$.

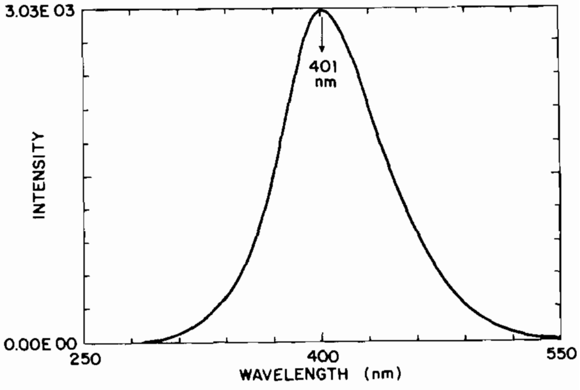

Fig. 7. 20 mA/40 kVp (Mo) X-ray excited emission spectrum of $LuTa_{0.99}Nb_{0.01}O_4$.

were made with these phosphors, using about 6 weight% of a methylmethacrylate type binder. A series of screens with varying thicknesses made with the composition $LuNb_{0.03}Ta_{0.97}O_4$ yielded the following speeds relative to HI PLUS-type $CaWO_4$ (~180 μ) = 1.0:

	Thickness (μ)				
	40	60	103	130	190
Speed at 30 kVp (Mo)	1.39	1.66	1.65	1.60	1.50
Speed at 70 kVp (W)	0.85	0.95	1.75	2.52	2.61

With the soft and more absorbing Mo radiation saturation occurs around 100 μ, while the brightness increases with the more penetrating and harder W radiation up to 190 μ, although here too, saturation clearly begins to set in. It is interesting to note that $YTa_{0.98}Nb_{0.02}O_4$, currently used in Du Pont's Cronex® Quanta Fast Detail, yields a speed of about 1.90 for 187 μ of active layer. These preliminary data on $LuTaO_4$:Nb suggest that it could well be the basis for a new type of X-ray intensifying screen.

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