

## LETTER TO THE EDITOR

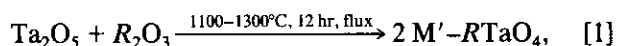
**M'-RTaO<sub>4</sub> Synthesis: Activation of the Precursor Oxides by the Reaction Flux**David B. Hedden,<sup>\*,1</sup> Charlie C. Torardi,<sup>†</sup> and William Zegarski<sup>\*</sup><sup>\*</sup>DuPont Company, Printing and Publishing, Patterson Boulevard, Towanda, Pennsylvania 18848; and <sup>†</sup>DuPont Company, Central Research and Development, Experimental Station, Wilmington, Delaware 19880-0356

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Studies of the M'-RTaO<sub>4</sub> (R = Gd, Y, Lu) phosphor synthesis reaction show that, contrary to previous views, the flux (e.g., Li<sub>2</sub>SO<sub>4</sub>, LiCl, Na<sub>2</sub>SO<sub>4</sub>) serves as an important reactant. Through a combination of techniques (DTA, TGA, XRPD, and mass balance), we find that close to its melting point, the flux reacts exothermically with the blended tantalum and yttrium oxides to give intermediate compounds. These reactive intermediates then combine to make M'-RTaO<sub>4</sub> and to regenerate the flux. Thus, the flux serves a dual purpose; it first activates the oxide reaction mixture and then serves as a classical flux in the growth of RTaO<sub>4</sub> crystals. In light of this discovery, a more appropriate term for these flux compounds is *catalyst* or *reactive flux* because they facilitate the synthesis of RTaO<sub>4</sub> through chemical reaction. © 1995

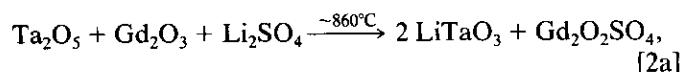
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Many solid state inorganic synthesis reactions are slow because they require the diffusion of nonvolatile materials before reaction can occur. In various cases, the low diffusion rates are compounded with low reactivities. Several general preparative techniques are commonly employed to increase reaction rates (1). The use of a flux that aids reactant diffusion and product crystal growth is a well-established method. Flux materials are often inorganic salts that melt below the reaction temperature, partially dissolve one or both of the reactants, do not participate in the solid state reaction, and do not react with the product (2). It has been believed that the flux used in the preparation of the commercially important monoclinic rare-earth tantalate X-ray phosphors M'-RTaO<sub>4</sub> (R = Y, Gd, Lu) behaves as defined above (3-6). In our investigations of the one-step synthesis of these compounds,

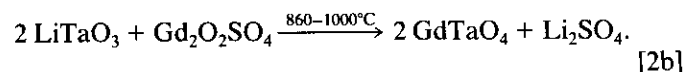
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we have discovered that the flux reacts with the constituent oxides to produce reaction intermediates. These intermediates are more reactive than the starting oxides. They combine to give the product, RTaO<sub>4</sub>, and to regenerate the flux (7, 8). In the absence of a flux, reaction of the oxides is sluggish and requires several firing/regrinding cycles for the synthesis of pure RTaO<sub>4</sub>. The new finding is important because modifications in RTaO<sub>4</sub> synthesis can have significant effects on the phosphor's luminescence behavior and effectiveness in medical X-ray imaging applications (9-14). Thus, an understanding of the reaction pathway may allow the design of rational approaches to changes in phosphor properties.

Flux materials used in Eq. [1] are group 1 sulfates (3-6), group 1 or 2 chlorides (3, 4), or eutectic mixtures (3, 15-18) of these salts. A typical example of intermediate phase formation is illustrated by the reaction of Gd<sub>2</sub>O<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub>, and Li<sub>2</sub>SO<sub>4</sub>. Crystallization of intermediates is indicated by the presence of a strong exotherm and no weight loss in a DTA/TGA trace (Fig. 1a). The exotherm could arise from a reaction of the oxides with molten Li<sub>2</sub>SO<sub>4</sub> since it is nearly coincident with the flux melting-point endotherm (860°C, Fig. 1b). No exothermic reaction occurs in the absence of any one of the three starting ingredients. X-ray powder diffraction (XRPD) analysis of quenched reaction samples (Fig. 2) shows that by 800°C, the starting oxides have been completely converted to the intermediate compounds LiTaO<sub>3</sub> and Gd<sub>2</sub>O<sub>2</sub>SO<sub>4</sub>,



and some of the desired M'-GdTaO<sub>4</sub> product,



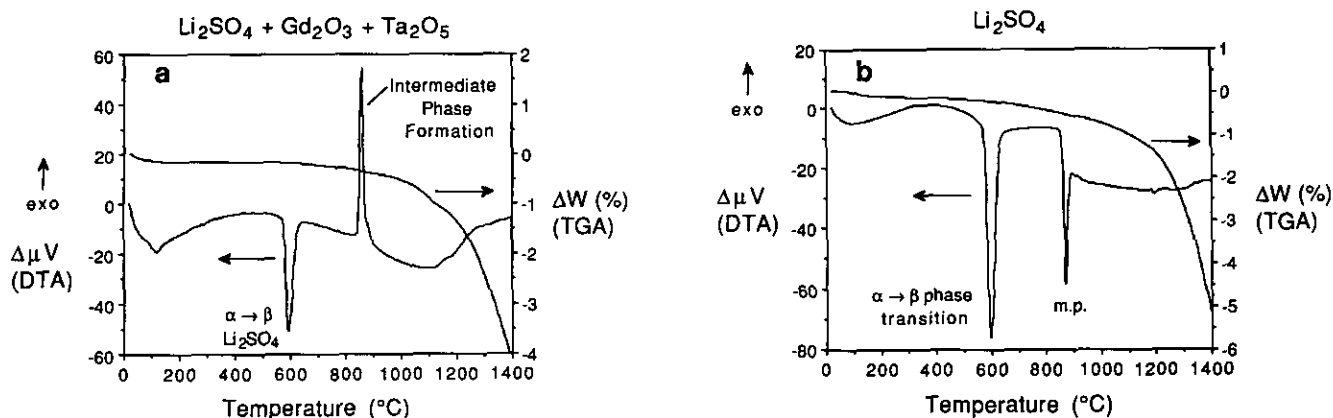


FIG. 1. DTA and TGA for (a) an equimolar mixture of  $\text{Li}_2\text{SO}_4$ ,  $\text{Gd}_2\text{O}_3$ , and  $\text{Ta}_2\text{O}_5$ , showing the exotherm arising from the formation of the intermediate compounds  $\text{LiTaO}_3$  and  $\text{Gd}_2\text{O}_2\text{SO}_4$ , and (b)  $\text{Li}_2\text{SO}_4$ , showing phase transition and melting-point endotherms.

High-temperature *in situ* XRPD analyses (19) show both intermediate phases to be crystalline materials. As the temperature is increased from 800 to 1000  $^{\circ}\text{C}$ , the intermediates react to complete  $\text{M}'\text{-GdTaO}_4$  formation and to regenerate  $\text{Li}_2\text{SO}_4$  (Eq. [2b]). At higher temperatures,  $\text{Li}_2\text{SO}_4$  behaves as a classical flux, assisting in the growth

of  $\text{GdTaO}_4$  crystals (4–12  $\mu\text{m}$ , the optimum size range for medical imaging applications). Sulfate ion concentration determination by ion chromatography of the final product mixture confirms the stoichiometry of Eq. [2b]. In addition, we observe that the  $\text{Li}_2\text{SO}_4$  inhibits decomposition of  $\text{R}_2\text{O}_2\text{SO}_4$  ( $R = \text{Gd}, \text{Y}, \text{Lu}$ ) to  $\text{R}_2\text{O}_3$  and  $\text{SO}_3$ . This further supports the reaction pathway (Eq. [2]) since decomposition of  $\text{R}_2\text{O}_2\text{SO}_4$  (20) would not result in the regeneration of  $\text{Li}_2\text{SO}_4$ .

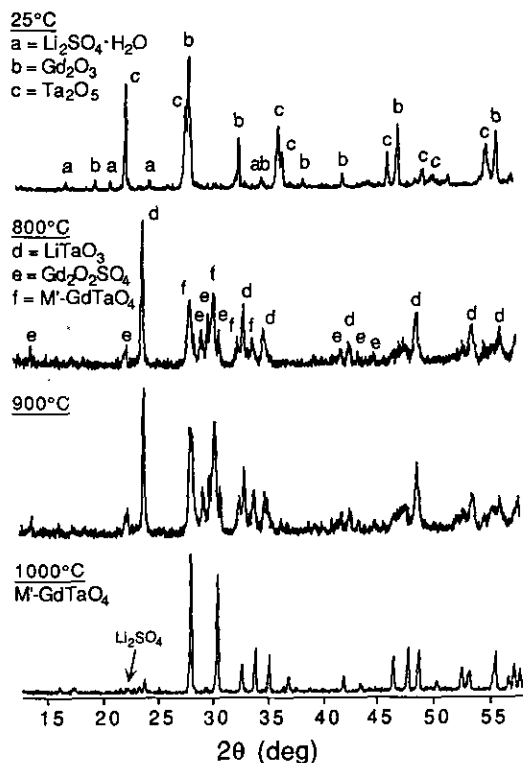
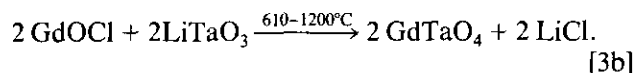
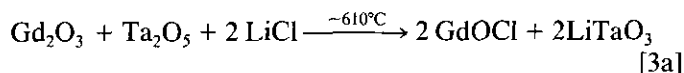


FIG. 2. X-ray powder diffraction patterns ( $\text{CuK}\alpha$ ) of an equimolar mixture of  $\text{Li}_2\text{SO}_4$ ,  $\text{Gd}_2\text{O}_3$ , and  $\text{Ta}_2\text{O}_5$  prior to heating, and of reaction samples quenched from 800, 900, and 1000  $^{\circ}\text{C}$  during the synthesis of  $\text{M}'\text{-GdTaO}_4$ .

DTA and XRPD studies of other  $\text{R}_2\text{O}_3/\text{Ta}_2\text{O}_5/\text{flux}$  reaction systems reveal similar intermediate phase formation (Table 1). Examples 1–8 show the subtle differences between the lithium, sodium, and potassium sulfate reactions. In the  $\text{Li}_2\text{SO}_4$  flux system,  $\text{LiTaO}_3$  is the only tantalate intermediate detected. However, in the sodium sulfate system, two tantalate intermediates are observed,  $\text{NaTaO}_3$  and  $\text{Na}_2\text{Ta}_4\text{O}_{11}$ . At higher temperatures, the latter compound is converted to  $\text{NaTaO}_3$ , which then reacts with  $\text{R}_2\text{O}_2\text{SO}_4$  to give  $\text{RTaO}_4$  and  $\text{Na}_2\text{SO}_4$ . With  $\text{K}_2\text{SO}_4$  flux, the only detected tantalate intermediate is  $\text{K}_2\text{Ta}_4\text{O}_{11}$ , and it reacts directly with  $\text{R}_2\text{O}_2\text{SO}_4$  to give  $\text{RTaO}_4$ . In all cases, the regenerated  $\text{M}_2\text{SO}_4$  ( $M = \text{Li}, \text{Na}, \text{K}$ ) can be recycled to continue the reaction.

With chloride fluxes, the formation of rare-earth oxychloride and metal-tantalate intermediates is illustrated by examples 9 and 10 in Table 1. The reaction pathway for example 9 is



When the eutectic mixtures given in Table 1 (examples

TABLE 1  
Intermediate Compounds Formed in the Flux Synthesis  
Reaction of  $M'-RTaO_4$  ( $R = Y, Gd, Lu$ )

Reaction mixture with $Ta_2O_5$	Flux mp <sup>a</sup> (°C)	Exotherm <sup>a</sup> (°C)	Intermediates
1. $Gd_2O_3/Li_2SO_4$	860	840	$LiTaO_3 + Gd_2O_2SO_4$
2. $Y_2O_3/Li_2SO_4$	860	850	$LiTaO_3 + Y_2O_2SO_4$
3. $Lu_2O_3/Li_2SO_4$	860	820	$LiTaO_3 + Lu_2O_2SO_4$
4. $Gd_2O_3/Na_2SO_4$	825	730	$Na_2Ta_4O_{11} + NaTaO_3 + Gd_2O_2SO_4$
5. $Y_2O_3/Na_2SO_4$	825	665	$Na_2Ta_4O_{11} + NaTaO_3 + Y_2O_2SO_4$
6. $Gd_2O_3/K_2SO_4$	1080	880	$K_2Ta_4O_{11} + Gd_2O_2SO_4$
7. $Y_2O_3/K_2SO_4$	1080	885	$K_2Ta_4O_{11} + Y_2O_2SO_4$
8. $Lu_2O_3/K_2SO_4$	1080	850	$K_2Ta_4O_{11} + Lu_2O_2SO_4$
9. $Gd_2O_3/LiCl$	590	545	$LiTaO_3 + GdOCl$
10. $Gd_2O_3/NaCl$	790	740	$Na_2Ta_4O_{11} + NaTaO_3 + GdOCl$
11. $Gd_2O_3/Li_2SO_4, K_2SO_4$ eutectic	517	610	$LiTaO_3 + Gd_2O_2SO_4$
12. $Gd_2O_3/Li_2SO_4, LiCl$ eutectic	475	500	$LiTaO_3 + Gd_2O_2SO_4$

<sup>a</sup> Melting points and exotherms are the onset temperatures from our DTA measurements. Samples were heated from 25 to 1500°C in air at a ramp rate of 20°C/min.

11 and 12) are used as the flux, the tantalum and rare-earth oxides selectively react with only one of the two possible anions or cations, and the temperature at which the intermediates are formed is lowered. In example 12, two rare-earth intermediates,  $GdOCl$  or  $Gd_2O_2SO_4$ , could form; only the latter is observed. In a similar vein,  $LiTaO_3$  is the only tantalate formed in example 11. Thus, the temperature ranges in which the intermediates are created, and where they react to give  $RTaO_4$ , may be controlled by judicious selection of the flux.

Observing only the initial reactants and final products of the  $RTaO_4$  reaction leads to the conclusion that compounds such as  $Li_2SO_4$  and  $LiCl$  act as conventional fluxes as described earlier. However, in light of the new discovery, they may be more appropriately described as *catalysts* or *reactive fluxes* because they facilitate the synthe-

sis of  $RTaO_4$  through chemical reaction. Looking ahead, this kind of chemistry may allow the facile synthesis of other solid state compounds that traditionally have been difficult to prepare.

#### ACKNOWLEDGMENTS

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