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Degradation of the holmium—barium—copper oxide superconductor, $HoBa_2Cu_3O_{6.92}$, under the action of H_2O and D_2O: a study by the radiothermoluminescence method

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Information about the existence of impurities and defects on the surfaces of high-T_c superconductors (HTSC) can be obtained by radiothermoluminescence (RTL).[1,2] The degradation of HTSC materials results from their interaction with water and CO_2:

$$2RBa_2Cu_3O_{7-x} + 3H_2O \rightarrow R_2BaCuO_5 + 3Ba(OH)_2 + 5CuO + (0.5-x)O_2,$$

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O,$$

where R is yttrium or a rare earth element.

It has been established that the intensity of RTL is very insignificant for freshly prepared HTSC or for samples stored in a dry atmosphere. However, a large increase in RTL intensity occurs if specimens are in contact with water.[3] Barium hydroxide, carbonate, and oxides make the largest contribution to RTL of superconducting ceramics with degraded surfaces. The RTL curves for $Ba(OH)_2$ and $BaCO_3$ differ slightly from each other,[3] which makes it difficult to estimate the contribution of each of them to the luminescence observed.

An isotope effect, manifested by the difference in the shapes of the RTL curves for specimens of $HoBa_2Cu_3O_{6.92}$ treated with hot H_2O or D_2O (Fig. 1, curves *1* and *2*, respectively) was observed in this work. In the latter case, there is a peak at 155—160 K on the $\log I_{RTL}$ *vs.* T(K) curve. This peak is absent in the case of the ceramics in contact with H_2O. The isotope effect is more pronounced in the RTL curves of the model systems $Ba(OH)_2$ and $Ba(OD)_2$ (curves *3* and *4*, respectively). A well resolved peak is observed in the RTL curve of $Ba(OH)_2$ at 155—160 K, whereas in the case of

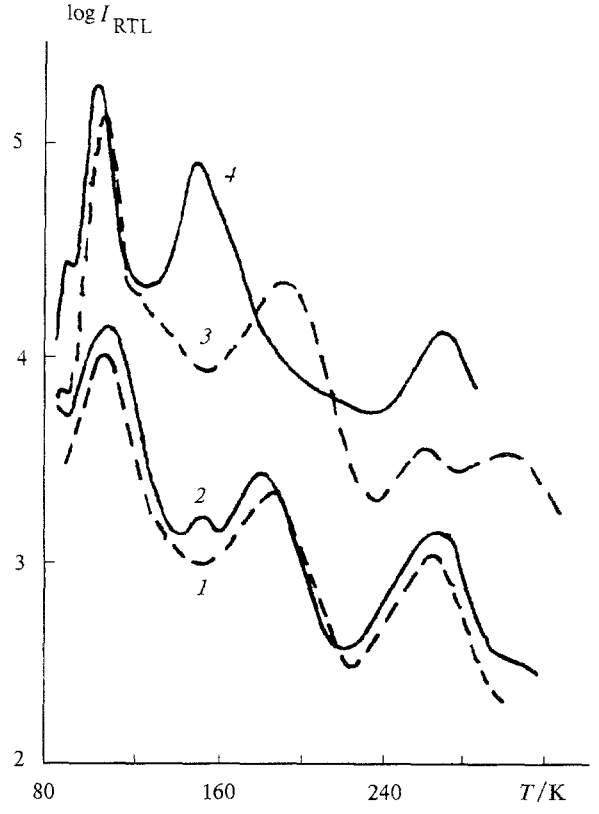

Fig. 1. Temperature dependence of the RTL of $HoBa_2Cu_3O_{6.92}$ in contact with H_2O (*1*) and D_2O (*2*), and the same for the RTL of $Ba(OH)_2$ (*3*) and $Ba(OD)_2$ (*4*) after their exposure to X-radiation (T = 77 K, E = 40 keV, absorbed dose 150 Gr, dose power 300 Gr h^{-1}).

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$Ba(OH)_2$ there is a minimum in this temperature range. Evidently, barium hydroxide contributes the most to the RTL of the degraded HTSC.

The nature of the observed isotope effect is not quite clear. As has been previously shown,[4] the maximum in the emission spectrum of the photochemically excited $Ba(OH)_2 \cdot 2H_2O$ (λ_{exc}= 253.7 nm, at 77 K) is at 400 nm, and its phosphorescence lifetime amounts to 2.0 sec (according to our data, the RTL maximum of $Ba(OH)_2$ lies in the 360—380 nm range). Earlier,[4] from experiments on the quenching of photoluminescence and from theoretical calculations, it was concluded that it is the hydroxide ion excited to the lower triplet level that acts as the luminescence-emitting species. We believe that electronically excited $*OH^-$ or $*OD^-$ ions may also be RTL emitters in the case of $Ba(OH)_2$ or $Ba(OD)_2$.

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Highly stereoselective catalytic phosphorylation of 2-(trimethylsilylmethyl)-1-(perfluorobutyl)ethanol by aryl methylchlorophosphonates

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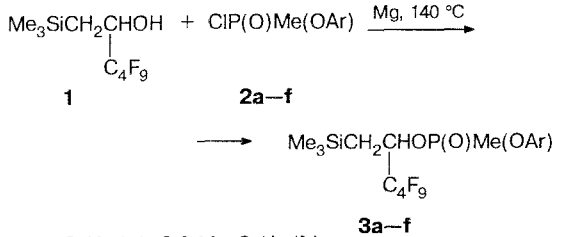
We have established that the catalytic phosphorylation of 2-(trimethylsilyl)-1-(perfluorobutyl)ethanol (**1**) by *O*-aryl(methyl)chlorophosphonates (**2a—f**) results in the formation of the corresponding esters of methylphosphonic acid (**3a—f**). According to the data of ^{31}P NMR and GLC, these products are mixtures of two diastereomers.



Ar = C_6H_5 (**a**), 2,6-$Me_2C_6H_3$ (**b**), 3,5-$Me_2C_6H_3$ (**c**), 4-*t*-BuC_6H_4 (**d**), 4-ClC_6H_4 (**e**), 2,4-$Cl_2C_6H_3$ (**f**)

In all cases, the prevailing (up to 68 mass %) diastereomers resonate at higher fields in the ^{31}PNMR spectra and have longer retention times than their minor counterparts (Table 1).

The formation of unequal amounts of diastereomers was previously observed in the acylation of secondary

Table 1. Diastereomeric composition of phosphonates **3a—f**

Compound	Ratio of diastereomers	
	^{31}P NMR	GLC
3a	31 : 69	31 : 69
3b	16 : 84	19 : 81
3c	26 : 74	26 : 74
3d	27 : 73	28 : 72
3e	32 : 68	31 : 69
3f	29 : 71	31 : 69

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