Synthesis and Characterizations of Rare Earth Compounds $RE(HCO_2)_3(HNO_2)(H_2CO_2)$ (RE = Y, Tb, Dy, Ho, Er, Yb, Tm) *

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Abstract A series of novel inclusion compounds with compositions of $RE(HCO_2)_3(HNO_2)(H_2CO_2)$ (RE = Y, Tb, Dy, Ho, Er, Yb, Tm) were synthesized and structures were characterized by X-ray methods. The orthorhombic structure was shown to be a new type with a non-centrosymmetric space group (20) $C222_1$ by single crystal structure determinations. It is characterized by networks of rare earth centered square anti-prisms formed by eight oxygen atoms through bridging carbon and nitrogen atoms. The guest formic acid molecules H_2CO_2 are distributed inside the open tunnels along the crystallographic *a* axis. The magnetic susceptibility measurements show the heavy rare earth compounds follow the Curie-Weiss law and the calculated numbers of Bohr magnetons are consistent with the RE^{3+} ions. The yttrium compound shows very weak temperature independent paramagnetism.

Keywords: Rare earths, Formate, Synthesis, Structure, Magnetic property, NLO materials

Non-linear optical materials have been attracted many materials scientists and chemists for their important rote in modern laser technology. Among the many commercially available inorganic NLO materials, lithium formate is one in use. Up to now there are few rare earth based NLO materials although chemically there are no restrictions. Rare earth formates is one of the compound series which show nonlinear optical properties[1]. Here we report another series of novel rare earth formate inclusion compounds with potential NLO properties.

The title compounds were synthesized by solution methods. All the reactants used have the A. R. grade. The aqueous solution of the rare earth nitiate salts were mixed with ammonium formate solution or mixture of liquid ammonia and formic acid. The clear solutions were very well stirred and slowly evaporated under relatively mild condition at 80 ℃. Large sized transparent crystals were obtained by this method.

We have reported[2] the single crystal structure data for the representative compound $Y(HCO_2)_3(HNO_2)(H_2CO_2)$ solved by single crystal method and the detailed studies on other structures will be reported shortly. The unit cell parameters given in Table 1 were obtained by least-square refinement of the measured 2θ values of the X-ray powder diffraction lines by using Si (*a* = 0.543053 nm) as an internal standard and they follow the lanthanide contraction. The structure, shown in Fig. 1, is characterized by networks of rare earth centered square antiprisms formed by eight oxygen atoms through bridging carbon and nitrogen atoms. The guest

Table 1 Unit cell parametrs of $RE(HCO_2)_3(HNO_2)(H_2CO_2)$ phases

RE	*a*/ nm	*b*/ nm	*c*/ nm	*V*/ nm^3
Y	0.6664(4)	1.836(2)	0.8439(5)	1.0327(9)
Tb	0.6686(2)	1.8488(9)	0.8472(4)	1.0473(5)
Dy	0.6649(9)	0.843(3)	0.8451(9)	1.036(2)
Ho	0.6666(2)	1.8403(9)	0.8446(3)	1.0362(4)
Er	0.6641(2)	1.832(1)	0.8427(3)	1.0252(6)

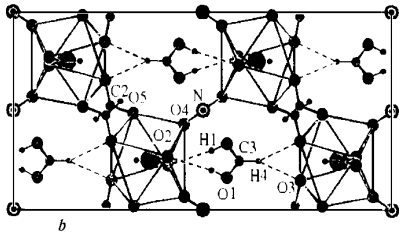

Fig. 1 [100] view of the orthorhombic $RE(HCO_2)_3(HNO_2)(H_2CO_2)$ structure

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Table 3 Cavity diameter of L^2 (nm)

O1—O3	0.4638(6)	O8—N2	0.4152(6)	O4—N1	0.4261(6)	O2—O4	0.3418(6)
O8—O10	0.4416(6)	O7—O9	0.4510(6)	O1—O4	0.2651(6)	O8—O9	0.2551(6)
O2—O3	0.3840(6)	O7—O10	0.4720(6)	O1—N3	0.4616(6)	O9—N2	0.4394(6)

europium ion and the role of the macrocycle decreases. The results of X-ray analysis give the shortest distance from the europium ion to the O atom in the azo-crown ether, i. e., Eu-O9, 0.5480(4) nm.

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formic acid molecules H_2CO_2 are distributed inside the open tunnels along the crystallographic *a*-axis and bounded to the network through weak hydrogen bonds.

The magnetic susceptibility data were collected on a vibrating magnetometer in the temperature range of 2～300 K. The results show that the heavy rare earth compounds follow the Curie-Weiss law and the calculated numbers of Bohr magnetons are 9.6, 11.0, 10.6 and 9.8 for Tb, Dy, Ho and Er respectively and they are consistent with the RE^{3+} ions (9.72, 10.63, 10.60 and 9.59 for Tb, Dy, Ho and Er respectively)[3]. The yttrium compound shows very weak temperature independent paramagnetism.

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