Synthesis, Characterization of a Novel Compound $SnEr_2O_4$

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(Received October 2, 2001; CL-010971)

A novel compound, a rare earth complex oxide $SnEr_2O_4$ was synthesized by the thermal decomposition of its oxalate precursor prepared by Rheological Phase Reaction Method. TG, IR, XRD and XPS were used to prove the formation of the compound $SnEr_2O_4$. The structure of $SnEr_2O_4$ was defined by Rietveld analysis. $SnEr_2O_4$ is cubic, *Pm*3*m*, $a = 7.3735$ Å, $V = 400.88$ Å^3, $Z = 4$, $D_x = 8.573$ g/cm^3, $D_m = 8.2$ g/cm^3.

In recent years, the research on rare earth became a focus, and a lot of new complex compounds with AB_2O_4 stoichiometry were prepared.[1–3] Compounds with the general formula AB_2O_4 in which A and B are metal ions exhibits many structure types. The major structural types are spinel, olivine, phenacite, K_2MgF_4, K_2SO_4, $CaFe_2O_4$. The $SnEr_2O_4$ compound exhibits full new structure that has not been reported.

$SnEr_2O_4$ was prepared by the thermal decomposition of the oxalate precursor that was prepared by Rheological Phase Reaction Method. Rheological Phase Reaction Method is a process of preparing compounds or materials from solid-liquid rheological mixture. That is, solid reactants were fully mixed in a proper molar ratio, made up by adding a proper amount of water or other solvents to a solid-liquid rheological body in which the solid particles and liquid substance were uniformly distributed. After reaction under suitable conditions, the product was obtained. Under the solid-liquid rheological state, many substances have new reaction properties.[4–9] SnO (AR), Er_2O_3(99.9%) and $H_2C_2O_4{\cdot}2H_2O$ are ground in molar ratio 1 : 1 : 4.1, and are placed into the reaction apparatus later. Then deionized water is added until rheological phase appears. The precursor was obtained after 10 h at 100 °C. Put it into a desiccator for future use.

The TG curve of the precursor was obtained by using a SHIMADZU DT-40 thermal analysis instrument in nitrogen atmosphere and raising the temperature at a steady rate of 20 °C/min. Figure 1 is the TG curve of the precursor. From the TG curve we know that at the decomposition temperature(825 °C) the precursor was completely decomposed to oxide, and we can see that the decomposition of the precursor is processed in 3 steps. In the first step, the crystal water was lost with the weight lost ratio of 5.524%(TG data); In the second step, $SnEr_2O_3CO_3$ was formed while in the last step $SnEr_2O_3CO_3$ was decomposed to complex oxide. The weight lost ratio in every step matches with that of calculation. The number of water in the precursor is three that is calculated by the weight lost ratio of water.

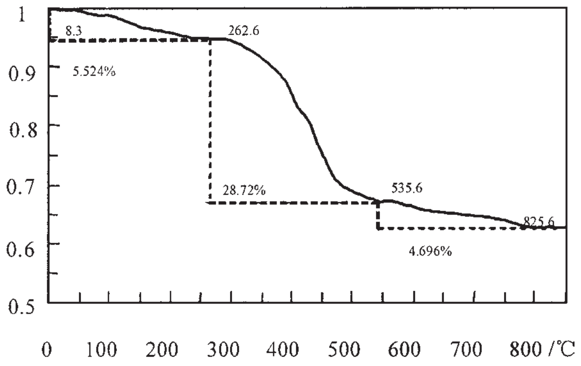

Figure 1. The TG plot of the precursor.

Grind the precursor and remove off superfluous $H_2C_2O_4$, and then place the precursor with a reaction boat into a quartz pipe, Raise the temperature to the decomposition point in nitrogen atmosphere and keep the temperature for 24 h. The $SnEr_2O_4$ is obtained.

From the data of thermal analysis, the thermal decomposition-mechanism of the precursor can be determined:[10]

$$SnEr_2(C_2O_4)_4{\cdot}3H_2O \rightarrow SnEr_2(C_2O_4)_4 + 3H_2O$$
$$SnEr_2(C_2O_4)_4 \rightarrow SnEr_2O_3CO_3 + 4CO + 3CO_2$$
$$SnEr_2O_3CO_3 \rightarrow SnEr_2O_4 + CO_2$$

The IR spectrum is obtained with a Nicoletsxb IR instrument within 400–4000 cm^{-1}. In the IR spectrum of the $SnEr_2O_4$, Er-O and Sn-O stretching vibrations are corresponding to 639.4, 572.8 and 511.2 cm^{-1} respectively.[10] They indicate that the precursor has been decomposed into oxide completely under the experiment conditions.

The powder specimen obtained was evaluated by X-rays diffraction(D/MAX-RA) with CuKα_1 radiation. Intensity data was collected in the range $20^\circ < 2\theta < 90^\circ$ using a step width of 0.02° and accounting period of 20 s at room temperature. $SnEr_2O_4$ is cubic, $a = 7.37348$ Å, $V = 400.88$ Å^3, $Z = 4$, $D_x = 8.573$ g cm^{-3}, $D_m = 8.2$ g cm^{-3}. The index data of the X-rays diffraction lists in Table 1.

In order to decide the valence of Sn in $SnEr_2O_4$, the XPS spectrum is measured with a XSAM800 XPS instrument. In XPS figure, the B. E. of Sn (3d) in the specimen is 486.2 eV that matches with the standard Sn(II) 3d-electron energy of 486.0 eV.

This work was supported by National Science Foundation of

Table 1. The index data of the X-rays diffraction

hkl	d_{OBS}(Å)	d_{CAL}(Å)	I/I_o
111	4.28537	4.27450	3
211	3.02743	3.02253	100
220	2.61816	2.61759	28
400	1.85109	1.85091	30
332	1.57939	1.57846	24
422	1.51230	1.51126	6
440	1.30922	1.30879	4
532	1.20084	1.20103	5
611		1.20103	
620	1.17023	1.17062	5
444	1.06805	1.06863	5

china (No. 20071026).

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