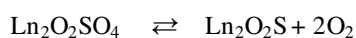11B/2006G360

Local Structure Analysis of Lanthanide Oxysulfate Having a Large- Capacity Oxygen Storage Property

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Introduction

In our previous studies, we demonstrated the large-capacity oxygen storage of lanthanide oxysulfates, $Ln_2O_2SO_4$, which uses sulfur as the redox center instead of metallic cations [1]. The following reaction between S^{6+} and S^{2-} attains the capacity of 2 mol-O_2 mol^{-1}, which is 8 times more than that of the conventional CeO_2-ZrO_2 materials.

$$Ln_2O_2SO_4 \quad \rightleftarrows \quad Ln_2O_2S + 2O_2$$

The redox property of $Ln_2O_2SO_4$ is dependent on Ln. The reduction and reoxidation of $Pr_2O_2SO_4$ started at lowest temperatures among Ln oxysulfates. To elucidate this Ln-dependence of redox property, the comparison is requested on the detailed structural aspect. In the present study, the effect of local structure of SO_4 unit of $Ln_2O_2SO_4$ on the redox property was investigated.

Experimental

$Ln_2O_2SO_4$ was synthesized by heating commercial $Ln_2(SO_4)_3 \cdot nH_2O$(Ln = La and Pr.) at 900 °C for 5h in air. The reduction and reoxidation properties were measured by thermogravimetry (TG, Rigaku 8120). The X-ray absorption fine structure (XAFS) of S K-edge was recorded on a BL-11B station of PF-KEK. A Ge(111) double-crystal monochromator was used. Spectral recording was performed at room temperature in the total electron/fluorescence electron yield. The XAFS data were processed using a REX 2000 program (Rigaku). The k^3-weighted EXAFS oscillation in the 3.0-13.0 Å^{-1} regions was Fourier-transformed. Phase shift and backscattering amplitude for S-O were obtained from the EXAFS data of Cs_2SO_4.

Results and Discussion

The reduction behavior of $La_2O_2SO_4$ and $Pr_2O_2SO_4$ was compared by measurering TG profiles up to 1000 °C in a stream of 5 % H_2/He. This was followed by cooling to room temperature in a stream of 5 % H_2/He and subsequent TG measurement in a stream of 2.5 % O_2/He to obtain the reoxidation behavior. The reduction and reoxidation of $Pr_2O_2SO_4$ started and completed at lower temperatures compared to the La compound.

To clarify the reason for such different redox behavior, it is of value to carry out studies on the structural aspect. The crystal structures of $Ln_2O_2SO_4$ can commonly be described by alternative sttacking of a $Ln_2O_2^{2+}$ layer and a sulfate (SO_4^{2-}) or sulfide (S^{2-}) as shown in Fig.1.
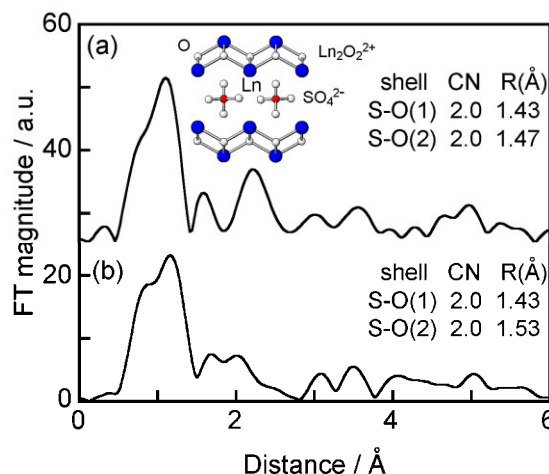

Fig.1 Fourier transforms of k^3-weighted S K-edge EXAFS for (a) $La_2O_2SO_4$ and (b) $Pr_2O_2SO_4$.

To obtain the detailed information of SO_4 tetrahedral unit, the local environment of S was investigated by EXAFS. Figure 1 shows the Fourier transforms of S K-edge EXAFS for $La_2O_2SO_4$ and $Pr_2O_2SO_4$. $La_2O_2SO_4$ showed a peak with a shoulder in the first neighboring shell. $La_2O_2SO_4$ were found to have two distinct S-O atomic distances. $Pr_2O_2SO_4$ showed more obvious difference in S-O atomic distances than $La_2O_2SO_4$. This result indicates a more distorted structure of the SO_4 tetrahedral unit in $Pr_2O_2SO_4$ rather than $La_2O_2SO_4$, which was agreement with the result from Rietveld analysis of XRD[1].

With an increase of the distortion in the tetrahedral SO_4^{2-}, the stability is expected to decrease. This is a possible structural reason for the lower reduction temperature of oxygen release form $Pr_2O_2SO_4$.

Acknowlededement

References

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