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Structure and magnetic properties of ternary potassium lanthanide oxides $KLnO_2$ (Ln = Y, Nd, Sm–Lu)

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Abstract

Crystal structures of ternary potassium lanthanide oxides $KLnO_2$ (Ln = Y, Nd, Sm–Lu) have been determined by powder X-ray diffraction using the Rietveld analysis method. All of the $KLnO_2$ compounds have the same hexagonal α-$NaFeO_2$ structure with space group $R\bar{3}m$. Magnetic susceptibility measurements for these compounds show paramagnetic behavior down to 1.8 K. The specific heat measurements indicate that the Gd, Dy, Ho and Er compounds have a magnetic anomaly at 1.1, 1.8, 1.2 and 0.8 K, respectively. The ^{151}Eu Mössbauer spectrum for $KEuO_2$ has been investigated at room temperature.

Keywords: Potassium lanthanide oxides; Triangular lattice; Magnetic susceptibility; Specific heat; Antiferromagnetic transition

1. Introduction

The oxides containing lanthanide ions have been attracting interest since they often show anomalous magnetic behavior at low temperatures. The most stable oxidation state of lanthanide ions is trivalent, and the electronic configuration of Ln^{3+} ions is [Xe] $4f^n$ ([Xe]: Xenon electronic core). Their magnetic properties are determined by the unpaired 4f electrons. They are highly localized electrons and the orbital contributions to their magnetic moments are significant. These features are in contrast with those of d electrons: the d orbitals are located in the valency shell and their orbital contributions to the magnetic moments are essentially quenched. Generally, the shielding by the surrounding 5s and 5p electrons in the outer shell makes the magnetic interactions between 4f electrons in condensed matters very weak, compared with those between d electrons. In fact, many of the lanthanide oxides order magnetically at the temperature lower than 4 K [1]. Among many magnetic studies on oxides containing lanthanide ions, the magnetic properties of alkali-metal lanthanide oxides are limited because of the difficulty in preparing these oxides [2].

The crystal structures of ternary alkali-metal lanthanide oxides have various types depending on the ionic radii of alkali-metal and lanthanide [3]. The crystal structures of lithium oxides have been grouped into four types [4,5]: α-type (space group: $I4_1/amd$), β-type (space group: $P2_1/c$), γ-type (space group: $Pbnm$) and δ-type (space group: $P2_1/c$), while those of sodium oxides have three types [6,7]: α-$LiFeO_2$ type (space group: $I4_1/amd$), β-$LiFeO_2$ type (space group: $C2/c$) and α-$NaFeO_2$ type (space group: $R\bar{3}m$). For potassium lanthanide oxides $KLnO_2$, however, only one type of hexagonal α-$NaFeO_2$ structure is observed because of the considerably smaller radii of Ln^{3+} ions (0.86–1.03 Å) compared with K^+ ion (1.38 Å) [3,8–10]. The schematic structure for the $KLnO_2$ compound is illustrated in Fig. 1. In this structure, the cation layers perpendicular to the c-axis are occupied alternatively by K^+ and Ln^{3+} ions. If the Ln^{3+} ion is magnetic, the Ln layers are magnetically separated by nonmagnetic K layers, and the Ln ions form a triangular lattice in the layers; thus, these compounds can be regarded as the two-dimensional (2D) triangular magnets. It is expected that they show unusual magnetic properties due to the magnetic frustration and/or low dimensionality [11–13].

We reported the crystal structures and magnetic properties of the ternary lithium lanthanide oxides $LiLnO_2$ and sodium lanthanide oxides $NaLnO_2$ in the previous papers [5,7]. In this paper, we have focused our attention on the crystal structure

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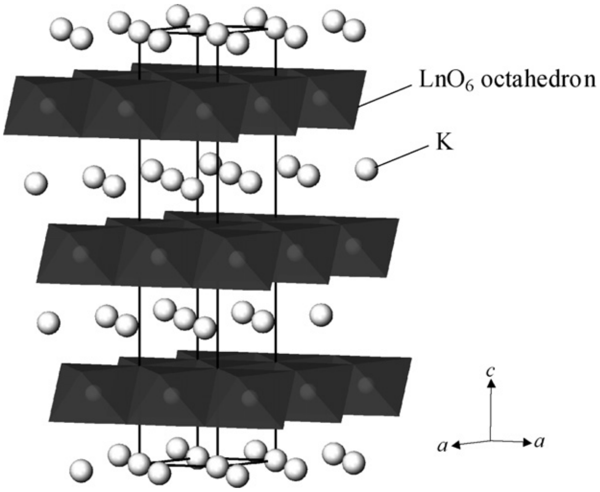

Fig. 1. The schematic crystal structure of $KLnO_2$.

and magnetic properties of ternary potassium lanthanide oxides $KLnO_2$ (Ln = Y, Nd, Sm–Lu) and studied them through powder X-ray diffraction, magnetic susceptibility and specific heat measurements. The ^{151}Eu Mössbauer spectrum for $KEuO_2$ has also been measured.

2. Experimental

Polycrystalline samples of $KLnO_2$ were prepared by the solid-state reaction. Starting materials of Ln_2O_3 (Ln = Y, Nd, Sm–Lu) and KO_2 (50% excess) were mixed and ground in an agate mortar in a glove box filled with argon gas. The mixtures were enclosed with a gold tube, and were sealed in an evacuated silica tube. Titanium monoxide TiO was also put in the silica tube in order to remove excess oxygen. Then, they were heated at 923 K for 16 h.

Powder X-ray diffraction measurements were performed at room temperature in the angle range of $10° \leq 2\theta \leq 120°$ at a 2θ step size of 0.02° with Cu Kα radiation on a Rigaku Multi-Flex diffractometer. The X-ray diffraction data were analyzed by the Rietveld technique, using the programs RIETAN2000 [14].

The ^{151}Eu Mössbauer spectrum was carried out on a Mössbauer spectrometer VT-6000 (Laboratory Equipment Co.) in the constant acceleration mode. The spectrometer was calibrated with a spectrum of α-Fe at room temperature. A $^{151}SmF_3$ radiation source (1.85 GBq) was used and the γ-rays were detected with a NaI scintillation counter. EuF_3 was used as a reference standard for the chemical isomer shift.

The temperature dependence of the magnetic susceptibilities was measured in both zero-field-cooled (ZFC) and field-cooled (FC) conditions under the applied magnetic field of 0.1 T in the temperature range of 1.8–300 K using a SQUID magnetometer (Quantum Design, MPMS-5S). The specific heats were measured using a relaxation technique with a commercial physical property measurement system (Quantum Design, PPMS model) in the temperature range of 0.5–15 K. The sample in the form of a thin plate was mounted on a sample holder with Apiezon for better thermal contact.

3. Results and discussion

3.1. Crystal structures

The $KLnO_2$ compounds were obtained as yellow to violet powders with small amount of unreacted KO_2 and Ln_2O_3. These compounds are very sensitive to moisture and will decompose in a few minutes when exposing them to the air. Powder X-ray diffractions show that all of the $KLnO_2$ compounds have the same hexagonal α-$NaFeO_2$ type structure (space group: $R\bar{3}m$). The powder X-ray diffraction pattern for $KLuO_2$ is shown in Fig. 2. Structural parameters and reliability factors for the $KLnO_2$ compounds prepared in this study are listed in Table 1.

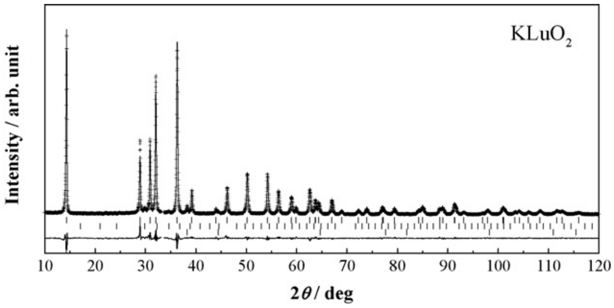

Fig. 2. Powder X-ray diffraction pattern for $KLuO_2$. The calculated and observed diffraction patterns are shown on the top solid line and cross markers, respectively. The vertical marks in the middle show the peak positions for $KLuO_2$, Lu_2O_3, and Au. The bottom trace is a plot of the difference between calculated and observed intensities.

Figs. 3 and 4 show the variation of lattice parameters and bond lengths against the ionic radius of Ln^{3+}, respectively. The lattice parameters increase with the ionic radius of the Ln^{3+} ion, and the Ln–O bond length also shows monotonous increasing. The K–O bond length is nearly constant (∼2.78 Å). These bond lengths are consistent with the lengths calculated from the Shannon's ionic radii [15]. Only for $KTbO_2$, the lattice parameters and Ln–O length somewhat deviate from this trend. This result may indicate that some Tb ions are oxidized to the tetravalent state.

3.2. ^{151}Eu Mössbauer spectrum

The ^{151}Eu Mössbauer spectrum for $KEuO_2$ measured at room temperature was shown in Fig. 5. Only a broad peak is observed, but actually it consists of the eight allowed transitions due to a quadrupole splitting of the ^{151}Eu nuclei (the nuclear spin: $I = 5/2$ and $I^* = 7/2$). The quadrupole Hamiltonian is given by:

$$H_{\text{quad}} = \frac{e^2qQ}{4I(2I-1)}[3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)]$$

Table 1
Structural parameters and reliability factors for $KLnO_2$

Compound	a (Å)	c (Å)	z (O)	R_{wp} (%)	R_I (%)
KYO_2	3.4492(3)	18.548(1)	0.2305(3)	11.60	4.44
$KNdO_2$	3.6043(8)	18.611(4)	0.2313(6)	14.05	3.76
$KSmO_2$	3.5690(2)	18.602(1)	0.2306(8)	15.78	5.85
$KEuO_2$	3.5415(4)	18.589(2)	0.2337(9)	16.76	5.01
$KGdO_2$	3.5114(6)	18.570(3)	0.2306(5)	13.36	4.96
$KTbO_2$	3.4644(3)	18.581(1)	0.2248(5)	14.39	3.17
$KDyO_2$	3.4737(4)	18.547(2)	0.2326(4)	11.63	2.28
$KHoO_2$	3.4486(3)	18.539(1)	0.2303(3)	9.30	2.20
$KErO_2$	3.4278(3)	18.527(1)	0.2288(3)	9.54	1.64
$KTmO_2$	3.4256(3)	18.516(2)	0.2268(3)	9.04	2.66
$KYbO_2$	3.4001(2)	18.497(1)	0.2286(2)	8.68	3.80
$KLuO_2$	3.3768(2)	18.502(1)	0.2288(2)	8.05	3.75

Note: space group $R\bar{3}m$, $Z = 3$; the atomic positions: K 3a(0, 0, 0); Ln 3b(0, 0, 1/2); O 6c(0, 0, z). Anisotropic atomic thermal parameters (B) were fixed to 0.6 Å^2 for K^+ and Ln^{3+} or 1.2 Å^2 for O^{2-}.