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Synthesis, structure and defects of rare earth chromates(v), $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y)

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Single phase zircon type rare earth (RE^{III}) chromates(v), containing Gd^{III}, Yb^{III} and Y^{III} ions, were synthesized by pyrolysis of the precursors prepared from the mixed solutions of RE^{III} and Cr^{VI} in the ratio of RE/Cr = 0.90/1.00. With other RE/Cr ratios, RE/Cr $\geqslant$ 0.95 or RE/Cr $\leqslant$ 0.85, the pyrolysis products contained a secondary phase of RE_2O_3 or Cr_2O_3. The composition of the compounds was determined to be $RE_{0.9}CrO_{3.85}$ by chemical analyses, with small standard deviations. The ESR spectrum of $Y_{0.9}CrO_{3.85}$ was typical of Cr^{V} ions in solids with $g = 1.968$ and $\Delta H = 140$ mT, and did not show the signals of Cr^{II} or Cr^{III}. These compounds have a defect structure which differs from other zircon type compounds containing RE^{III} of larger ionic radius than Gd^{III}. The detailed structure was determined by the powder X-ray Rietveld method. The measured densities suggested that the defect structure is $RE_{0.9}(CrO_4)_{0.85}(CrO_3)_{0.15}$ (RE = Gd, Yb and Y). Apparently this structure contains $CrO_3^{\bullet}$ with a dangling bond. Based on the structural analyses and *ab initio* MO calculations, these species might be stabilized by forming Cr_2O_7 (CrO_3–O–CrO_3) units in $RE_{0.9}CrO_{3.85}$ due to the oxygen sharing between $CrO_3^{\bullet}$ and the neighboring CrO_4 tetrahedron. The present results conclude that the phase diagram of rare earth chromate(v) series reported so far should be corrected so that the compounds containing Gd^{III} and smaller ions have the defect zircon type structure.

Introduction

Rare earth chromates, $RECrO_4$ (RE = La, Nd–Lu and Y) are one of the compound groups containing the unusual high valence state Cr^{V} ion, and stable in ambient atmosphere.[1–7] A number of studies have been carried out on the complex magnetic behavior of $RECrO_4$ due to the interaction between two kinds of magnetic ions, RE^{III} and Cr^{V}.[8–11] $RECrO_4$ compounds have been synthesized by (a) the reaction of $RE_2(CrO_4)_3$ with RE_2O_3 or $RE(NO_3)_3{\cdot}nH_2O$ at elevated temperatures,[1–5] (b) the thermal decomposition of $RECr(C_2O_4)_3{\cdot}nH_2O$ in air[6,7] or (c) the reaction of $Cr(NO_3)_3{\cdot}9H_2O$ with $RE(NO_3)_3{\cdot}6H_2O$ at elevated temperatures.[1–5] Schwarz, and Roy and Nag, have reported that $LaCrO_4$ has a monazite type structucture,[1,6] and other $RECrO_4$ containing Nd^{III} and smaller ions have a zircon type structure.[3–5]

In our previous work, we have reported that $RECrO_4$ (RE = La and Nd) can be synthesized as a single phase by pyrolysis of the precursor prepared from equimolar mixed solutions of RE^{III} and Cr^{VI} and have determined the detailed structure by X-ray Rietveld refinement.[12] $EuCrO_4$ was also obtained by the same procedure and structural parameters were determined.[13] By measurement of the electric conductivity, Seebeck coefficient and magnetic susceptibility, and from *ab initio* molecular orbital (MO) calculations, $RECrO_4$ (RE = La, Nd and Eu) was found to be an n-type semiconductor having a unique conduction band of antibonding $p\sigma^*$ states (O 2p origin) arising from the intermixing of Ligand to Metal Charge Transfer (LMCT) states.[13–17]

In the course of further investigations on $RECrO_4$ containing smaller RE^{III} ions than Eu^{III}, however, we found that these compounds were never obtained as the stoichiometric ones reported so far. When we started the synthesis from the precursor of stoichiometric composition, it always produced a mixed phase. Single phase compounds were obtained only from non-stoichiometric precursors. So, the structure and composition of the rare earth chromates(v) containing smaller RE^{III} ions than Eu^{III} must be corrected.

In the present work, rare earth chromates(v) containing Gd^{III}, Yb^{III} and Y^{III} ions were synthesized by our method. For the products obtained as a single phase, the composition and valence state of chromium were investigated by chemical analyses and electron spin resonance (ESR), and the defect structure and structural parameters were determined by pycnometry and the X-ray Rietveld method. The structural stability of the compounds was discussed based on the structural analysis and *ab initio* MO calculations.

Experimental

Compounds can be synthesized by pyrolysis of the precursor at 853 K for 3 h in air for $NdCrO_4$ and 863 K for 1 d in O_2 for $EuCrO_4$: the precursors were prepared by vacuum drying of the equimolar solutions of $Nd(CH_3COO)_3$ or $Eu(CH_3COO)_3$, and CrO_3 at 343 K, followed by preheating at 673 K in air, as reported previously.[12,13] The same procedure was applied for synthesis of the rare earth chromates(v) containing Gd^{III}, Yb^{III} and Y^{III}. The precursors were prepared from solutions of $RE(CH_3COO)_3$ (RE = Gd, Yb or Y, 99.9% pure reagent) and CrO_3 (reagent grade), the metal concentrations being determined by chelatometry and redox titration. The mole ratio of RE/Cr in the precursor was systematically arranged as 1.00/1.00, 0.95/1.00, 0.90/1.00, 0.85/1.00, 0.80/1.00 and 0.50/1.00. Hereafter, these precursors are referred to as RE100, RE95, RE90, RE85, RE80 and RE50 (RE = Gd, Yb and Y), respectively. Pyrolysis conditions of the precursors to form single phase rare earth chromates(v) were investigated by thermogravimetry and differential thermal analysis (TG–DTA) and X-ray diffraction (XRD).

The chemical composition of the rare earth chromates

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prepared as a single phase was determined by titration. About 0.5 g of a sample was dissolved in 100 cm^3 of 10 mol dm^{-3} H_2SO_4 solution. Rare earth chromate(V) dissolves into a sulfuric acid solution by the disproportionation reaction of Cr^V ions, as follows:

$$3Cr^{V} \rightarrow 2Cr^{VI} + Cr^{III} \quad (1)$$

Sodium sulfuric peroxide was added to oxidize the formed Cr^{III} ions to chromate ions, and then the total concentration of chromium was determined by conventional redox titration with an Fe^{II} solution. The concentration of rare earth ions was determined by chelatometry with an EDTA solution: prior to this titration chromate ions must be reduced by addition of H_2O_2 to prevent decomposition of EDTA chelates.

X-Ray diffraction patterns were measured by a JEOL rotating anode diffractometer with a monochromator under the following conditions: Cu Kα, 30 kV, 300 mA; scanning step, 0.02° (2θ); counting time, 20–25 per step. The XRD data were collected in the 14–114° 2θ range. Structure refinement by the Rietveld method was carried out using the RIETAN program.[18,19] The peak shape was represented by a pseudo-Voigt function.[19] The atomic scattering factor and dispersion correction for Cr^V were assumed to be the same as those of the Cr atom,[19] since they are not available. The densities of the compounds were measured in CCl_4 using a liquid pycnometer.

X-Band electron spin resonance (ESR) measurements were carried out at 77 K using a JEOL ESR-1500 spectrometer. The applied frequency was 9.2 GHz.

Ab initio molecular orbital (MO) calculations at the MP2 level[20] were carried out to calculate the potential energy of a $Cr_2O_7^{4-}$ ($(CrO_3–O–CrO_3)^{4-}$) cluster, where the position of the centered oxygen atom was changed and the positions of the six terminal oxygen atoms were fixed. The basis sets of 6-311+G* were applied to both atoms.[20] The Madelung potential was also taken into account, and point charges of +3, +5 and −2 were placed on Nd, Cr and O sites, respectively, within a sphere of 0.6 nm radius from the center of mass in the $Cr_2O_7^{4-}$ clusters. In total, eight trivalent charges were used for Nd^{3+} cations, six pentavalent charges for Cr^{5+} cations and twenty-four negative divalent charges for O^{2-} anions. All calculations were performed using the GAUSSIAN98 program.[20]

Results and discussion

Synthesis of single phase $RECrO_4$ (RE = Gd, Yb and Y)

Significant differences were not observed in the thermal decomposition behavior of RE100, RE95, RE90, RE85, RE80 and RE50. There was an intermediate plateau in the region of 813–1013 K in the TG curves and an endothermic peak appeared around 813 K in the DTA curves in O_2 atmosphere. Based on the TG–DTA data, pyrolysis at constant temperatures around 833 K in O_2 atmosphere was carried out to determine the conditions for the preparation of single phase compounds (by XRD).

Fig. 1 shows the XRD patterns for the pyrolysis products of precursors at 833 K for 1 d in a flow of O_2. As shown in Fig. 1(a), the main peaks could be indexed to a tetragonal zircon-type structure for all RE/Cr ratios. The precursor Yb100 was expected to produce zircon-type $YbCrO_4$ as a single phase. However, the pyrolysis product of Yb100 was not a single phase, since small amounts of Yb_2O_3[21] were observed as shown in Fig. 1(b). Under any oxygen pressure, PO_2, from 0 to 1 atm, the products from Yb100 contained Yb_2O_3 as a secondary phase but no Cr_2O_3 was formed. This suggests that the Yb content of Yb100 was too high to form a single phase of ytterbium chromate. Fig. 1(b) shows that the pyrolysis product from Yb95 also contains small amounts of Yb_2O_3. In contrast, Yb_2O_3 was not detected in the products from Yb85, 80 and 50, but Cr_2O_3 was formed as a secondary phase.

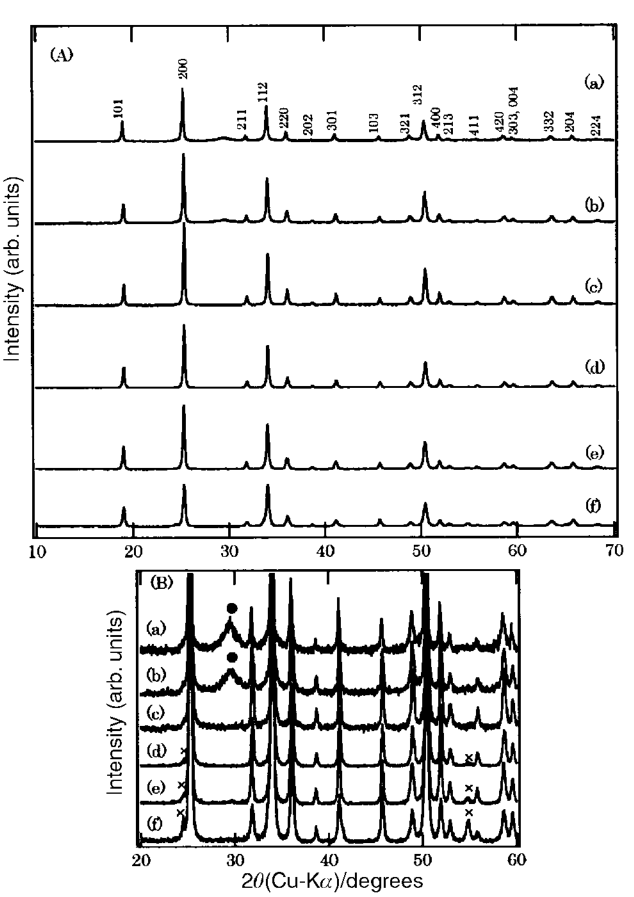

Fig. 1 XRD patterns of the pyrolysis products from Yb precursors, (a) Yb100, (b) Yb95, (c) Yb90, (d) Yb85, (e) Yb 80 and (f) Yb50 at 833 K for 1 d in O_2. In (A), the *hkl* indexing was done by the zircon-type structure, and in (B), the peaks indicated by ● and × are identified as Yb_2O_3 and Cr_2O_3.

Consequently, only the product from Yb90 was a single phase of ytterbium chromate, and all diffraction peaks were completely indexed to the zircon-type structure, as shown in Fig. 1(a). Exactly the same results were obtained with Gd and Y, as shown in Fig. 2(a) and (b): for $RE/Cr \geqslant 0.95$ small amounts of RE_2O_3 were formed, and for $RE/Cr \leqslant 0.85$ Cr_2O_3, by the pyrolysis at 843 K for 1 d in a flow of O_2. Accordingly, the products from RE90 (RE = Gd, Yb and Y) were annealed further in an O_2 atmosphere with grinding every two days, in order to prepare well-crystallized samples. The most suitable conditions determined are listed in Table 1.

The chemical compositions of rare earth chromates thus prepared were determined, with small standard deviations, as shown in Table 1. The RE/Cr ratio coincides with that of the precursors. Analytical values in Table 1 indicate that single phase compounds have the average composition of $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) and the nominal valence of chromium is five.

The ESR spectrum of $Y_{0.9}CrO_{3.85}$ showed a broad line width, Δ*H*, of 140 mT and a *g*-value of 1.968, as shown in Fig. 3. The spectrum is in agreement with those of $LaCr^{V}O_4$[6] and $K_3Cr^{V}O_8$;[23] these compounds have Cr^V ions (d^1 configuration) and show a short spin–lattice relaxation time and hence broad line width.[24] No traces of other valence states, such as Cr^{III} and Cr^{II}, are observed in the spectrum. A well resolved ESR spectrum of Cr^V cation could not be measured in $Gd_{0.9}CrO_{3.85}$ and $Yb_{0.9}CrO_{3.85}$ because of interference from Gd ($4f^7$) and Yb ($4f^{13}$) atoms but the results from chemical analyses and ESR support that the chromium atoms in $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) are pentavalent.

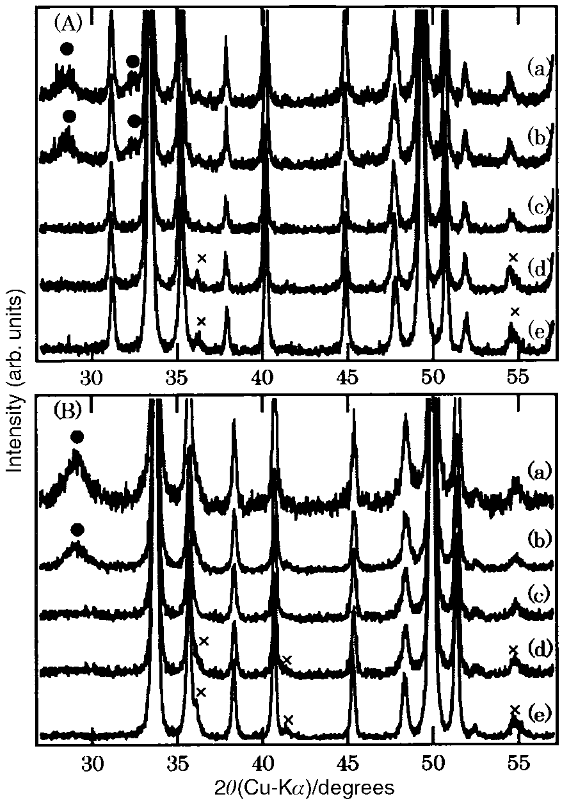

Fig. 2 XRD patterns of the pyrolysis products from (A) Gd and (B) Y precursors, (a) RE100, (b) RE95, (c) RE90, (d) RE85 and (e) RE 80 at 843 K for 1 d in O_2. The peaks indicated by ● and × are identified as RE_2O_3 and Cr_2O_3.

Table 1 Pyrolysis conditions in O_2 and chemical compositions of single phase rare earth chromates, prepared from RE90 (RE = Gd, Yb and Y). The values within parentheses indicate the standard deviations of the final figure

	Gd	Yb	Y
Conditions			
Temperature/K	843	833	843
Time/d	10	8	10
Composition	$Gd_{0.891(2)}$-$Cr_{1.00(1)}O_{3.839(4)}$	$Yb_{0.906(2)}$-$Cr_{1.00(1)}O_{3.859(2)}$	$Y_{0.897(1)}$-$Cr_{1.00(1)}O_{3.846(2)}$
Valence state of Cr	+5.01	+5.02	+4.99

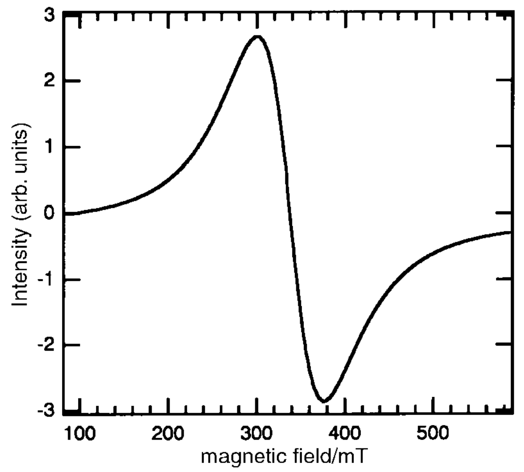

Fig. 3 ESR spectrum of Cr^V in the defect zircon-type $Y_{0.9}CrO_{3.85}$ structure at 77 K.

Structure of nonstoichiometric $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y)

Taking into account the zircon-type structure, two defect models for $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) are possible. Model I is that oxide ions on 16h sites are defects to compensate the loss of positive charges, producing $CrO_3^{\bullet}$ with a dangling bond, in turn. Accordingly, Model I involves two kinds of vacancies, rare earth and oxygen, expressed as $RE_{0.9}(CrO_4)_{0.85}(CrO_3^{\bullet})_{0.15}$. Model II is that some Cr^V ions occupy rare earth sites, and oxygen defects are not formed. Therefore, Model II involves small amounts of rare earth vacancies, and compounds are described as $RE_{0.90}Cr_{0.0375}(CrO_4)_{0.9625}$ or $(RE,Cr)_{0.974}CrO_4$. When all the diffraction peaks are indexed as the zircon-type structure as shown in Fig. 1, for example, the lattice constants, *a* and *c*, can be determined by XRD measurements with an internal standard of Si. Experimentally determined lattice constants and the theoretical density for each model of $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) are listed in Table 2, together with measured densities. It is clear that the measured densities of $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) are in good agreement with those of Model I, that is, $RE_{0.9}(CrO_4)_{0.85}(CrO_3^{\bullet})_{0.15}$. The $CrO_3^{\bullet}$ species are usually unstable and rare in solids.[25] In addition, the charge imbalance created by aliovalent substitution in $Nd_{1-x}Ca_xCrO_4$ was found to be compensated by the oxidation of Cr^V to Cr^{VI}, and not by oxygen defects.[14] Therefore, the defect structure of $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) found in the present work is unusual. Stabilization of these compounds is discussed later.

The Rietveld structural refinement was carried out based on Model I for the defect zircon-type structure (S.G. $I4_1/amd$, tetragonal); the rare earth atoms occupy 4a (0, 3/4, 1/2), chromium atoms 4b (0, 1/4, 3/8) and oxygen atoms 16h (0, O_y, O_z). On refinement, $NdVO_4$ was used as a starting model for the initial oxygen positions and thermal parameters, which were determined by neutron diffraction,[26] and isotropic thermal parameters, B_{eq}, were employed. Initially, site occupancies were fixed to the values found from chemical analysis in Table 1 for the refinement of other parameters, and at the final stage the site occupancies were also refined. The final Rietveld profiles for $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) are shown in Fig. 4. The refined crystallographic data together with reliability factors are given in Table 3. For all samples, the reliability factors (R_{wp}, R_p, R_F and R_{exp}) are sufficiently small, and *GOF* (goodness of fitting indicator: R_{wp}/R_{exp}) is less than the required limit of 1.3, except for 1.32 found for the yttrium compound. The isotropic thermal displacement parameters B_{eq} for Cr atoms are relatively high in every $RE_{0.9}CrO_{3.85}$ sample, in comparison to those for RE atoms. This is reasonably attributed to the approximation used here, that is, the atomic scattering factor of neutral Cr atoms may be larger than that of Cr^V ions. The values in Table 3 indicate that the structural refinements converged well. The calculated densities by Rietveld refinement of $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) were the same as those in Table 2. The selected bond lengths

Table 2 Calculated and observed densities in g cm^{-3}, and lattice constants in nm of $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y)

	$Gd_{0.9}CrO_{3.85}$	$Yb_{0.9}CrO_{3.85}$	$Y_{0.9}CrO_{3.85}$
Density (calc.)/g cm^{-3}			
Model I	5.18	5.82	4.07
Model II	5.39	6.04	4.23
Density (obs.)/g cm^{-3}	5.07	5.79	4.10
Lattice constants[a]/nm			
a	0.7197	0.7038	0.7109
c	0.7109	0.6205	0.6280

[a] Determined by XRD measurements using the internal standard of Si powder.

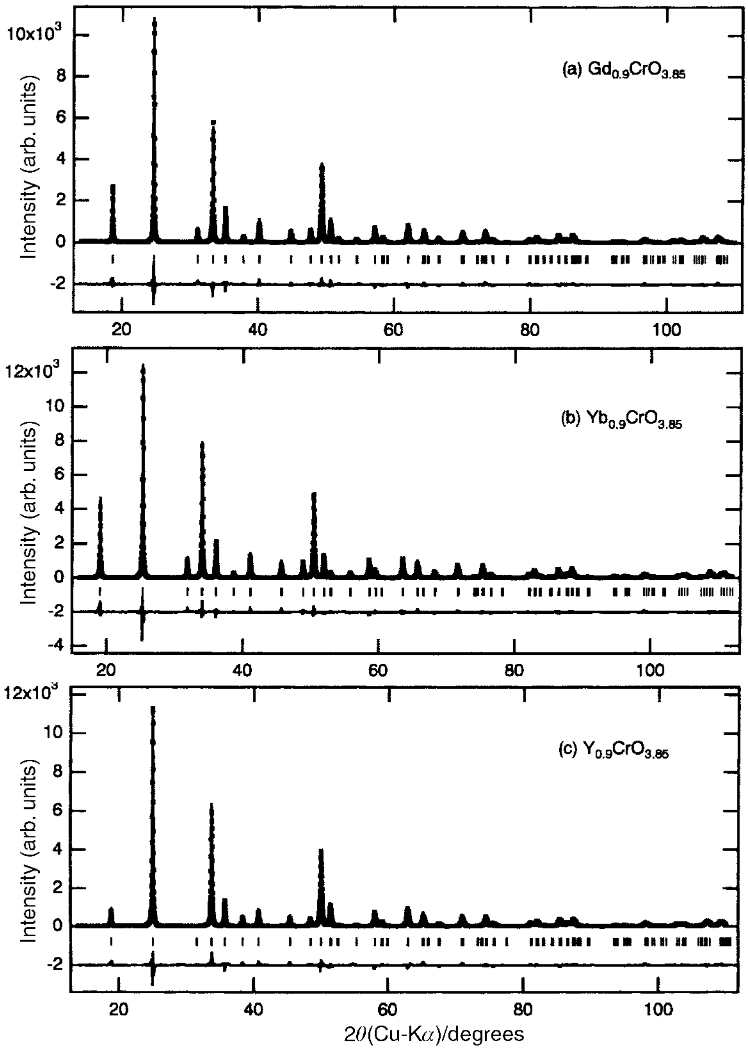

Fig. 4 The final Rietveld profiles of defect zircon type $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y). Solid lines and dots indicate the observed and calculated diffraction patterns, respectively. The stick marks show the positions of allowed Bragg reflections and the traces at the bottom show the difference between the observed and calculated intensities at each step.

and angles are summarized in Table 4. The results of Rietveld structure refinement support that $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) is a single phase of the defect zircon-type oxide with rare earth and oxygen vacancies.

Table 3 Crystal data for the defect zircon-type $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) structure refinement

	$Gd_{0.891}Cr_{1.00}O_{3.839}$	$Yb_{0.906}Cr_{1.00}O_{3.859}$	$Y_{0.897}Cr_{1.00}O_{3.846}$
No. of reflections	130	125	127
Lattice constants/nm			
a	0.71974(1)	0.70376(1)	0.71092(1)
c	0.63104(1)	0.62051(1)	0.62796(1)
Site occupancy, g^a			
RE (4a)	0.905(2)	0.906(2)	0.917(4)
O (16h)	0.968(4)	0.950(4)	0.950(5)
Coordinates of O atoms			
O_y	0.4365(6)	0.4423(5)	0.4406(7)
O_z	0.1977(4)	0.1963(4)	0.1960(6)
B_{eq}/Å^2			
RE (4a)	0.085(2)	0.037(2)	0.102(3)
Cr (4b)	0.91(2)	0.90(2)	1.02(3)
O (16h)	1.21(2)	0.99(2)	1.23(4)
R-factors			
R_{wp}	11.31	10.57	13.29
R_p	9.42	8.47	9.54
R_I	4.11	4.10	5.25
R_F	2.52	2.12	3.09
GOF	1.30	1.28	1.32

[a] g for Cr atom on the 4b site was fixed to 1.00.

As reported in our previous papers, $NdCrO_4$ has the normal zircon-type structure,[12] as does $EuCrO_4$.[13] The present results suggest that rare earth chromates(V) containing smaller ions than Eu^{III}, namely trivalent ions of atomic number 64–71 and Y^{III}, are expected to form the defect zircon-type compound, since $_{64}$Gd is an adjacent element to $_{63}$Eu in the lanthanide series. So far, however, no such structure has been reported for rare earth chromates(V), as summarized in Table 5. We attempted to prepare ytterbium chromate(V) by the method reported by Schwarz, using $Cr(NO_3)_3 \cdot 9H_2O$ and $Yb(NO_3)_3 \cdot 6H_2O$.[5] The XRD patterns of the products thus prepared showed the existence of a secondary phase of Yb_2O_3, the same result as that from Yb100 in Fig. 2(b). The signal to noise ratio of the XRD patterns of $YCrO_4$[4] and $DyCrO_4$[5] reported by Schwarz was not good, so that there is every possibility of overlooking small amounts of secondary phase. The XRD patterns for the compounds of atomic number 64, 65 and 67–71 were not shown in his paper.[5] In the neutron diffraction patterns of $DyCrO_4$ reported by Steiner *et al.*[10] it is possible to recognize a small peak between the 200 and 211 peaks, which may correspond to Dy_2O_3, though the signal to noise ratio was not very good. Buisson *et al.*[9] reported $TbCrO_4$ but the sample was not well crystallized and there were a few unindexed peaks in the XRD pattern.

The fact that single phase compounds are not obtained from

Table 4 Selected bond lengths, angles and inter-atomic distances in $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y)

	$Gd_{0.9}CrO_{3.85}$	$Yb_{0.9}CrO_{3.85}$	$Y_{0.9}CrO_{3.85}$
Cr–O/nm	0.1743(3) × 4	0.1749(3) × 4	0.1757(4) × 4
RE–O/nm	0.2439(7) × 4	0.2410(6) × 4	0.2410(8) × 4
	0.2394(6) × 4	0.2211(6) × 4	0.2211(8) × 4
Shortest O–O/nm	0.2657(5)	0.2569(5)	0.2591(7)
O–Cr–O/°	100.4 × 2	101.4 × 2	100.9 × 2
	114.2 × 4	113.7 × 4	113.9 × 4

the precursors having stoichiometric compositions was also observed by another group working on the magnetic properties of these compounds.[28] Accordingly, our results on the phase of rare earth chromate compounds are summarized as shown in Table 5.

Stability of $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) based on the structural analysis

As shown in Fig. 5, the lattice constants, *a* and *c*, decrease almost linearly with decreasing ionic radius of RE^{III} ions, r_{RE},[27] but in detail the linearity is not perfect. Hereafter, the data for $NdCrO_4$ and $EuCrO_4$ are those cited from our previous work.[12,13] Rare earth chromates(v) exhibit the lanthanide contraction, though the compound structure changes from normal to the defect zircon type at the boundary between Eu^{III} and Gd^{III}. Generally the *y*-coordinate of oxygen, O_y, increases, and the *z*-coordinate, O_z, decreases with decreasing r_{RE}, but there is a clear gap for the change of each parameter between Eu^{III} and Gd^{III}, as shown in Fig. 6. Fig. 7(a) and (d) represent the 100 planes of $EuCrO_4$ and $Gd_{0.9}CrO_{3.85}$, respectively. This plane reflects a feature of the zircon-type structure and is useful for discussion of the structural change of this type.[14] With decreasing r_{RE} the RE–O distance decreases, so that the 16h site oxygen atom must change position to the direction of the solid arrow indicated in Fig. 7(b). This shift is reflected in the general trend in Fig. 6 that O_y increases and O_z decreases as shown by broken arrows in Fig. 7(b). The magnitude of the shift, however, changed suddenly between Eu^{III} and Gd^{III}. This indicates that the equivalent position of 16h oxygen markedly shifts in $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y), as shown in Fig. 7(c), leading to elongation of the Cr–O bond and a decrease of the nearest O–O distance between CrO_4 units. This change can be shown numerically, as plotted in Fig. 8: the calculated Cr^V–O bond length from crystal radii of Cr^V (0.049 nm, C.N. 4)[27] and O^{2-} (0.121 nm, C.N. 2)[27] is also shown. The Cr^V–O bond length of stoichiometric $RECrO_4$ (RE = Nd and Eu) agrees with the calculated one but that of non-stoichiometric $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) is much larger. The nearest O–O distance of $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) is shorter than the sum of ionic radii for two O^{2-} ($2 \times 0.135 = 0.270$ nm, C.N. 2)[27] but longer than that of the crystal radii (0.242 nm). Since too much elongation of the Cr–O bond in the $CrO_4{}^{3-}$ tetrahedron adversely affects the stability of the compounds,[12] there must be an unusual configuration of oxygen atoms in $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y).

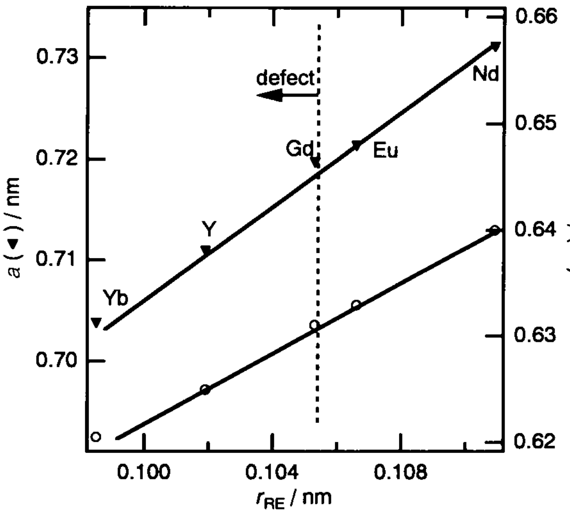

Fig. 5 Plot of lattice constants of the zircon-type rare earth chromates(v), as a function of ionic radius of RE^{III} ions, r_{RE} (RE = Nd, Eu, Gd, Yb and Y).

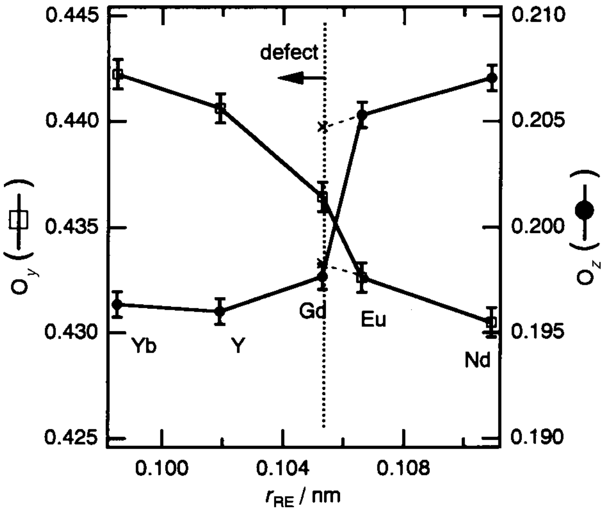

Fig. 6 Plot of *y*- and *z*-coordinates of 16h oxygen in zircon type rare earth chromates(v) as a function of the ionic radius of RE^{III} ions, r_{RE}. × indicates the values for $Gd_{0.9}CrO_{3.85}$ by extrapolation with the data of $NdCrO_4$ and $EuCrO_4$.

From the above results, the following scheme for how $CrO_3{}^{\bullet}$ are stabilized in $RE_{0.9}CrO_{3.85}$ can be drawn. The species, such as $SiO_3{}^{\bullet}$, having a dangling bond tends to attract an oxygen atom from outside or the neighboring SiO_4 units to form a new Si–O bond.[25] Therefore, it may be possible that in the oxygen-deficient part of $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) the 16h oxygen position in Fig. 7(c) may change to the one shown in Fig. 7(e) to share an oxygen atom between $CrO_3{}^{\bullet}$ and the neighboring CrO_4 tetrahedron. With this model the defect compounds can be expressed as $RE_{0.9}(CrO_4)_{0.7}(Cr_2O_7)_{0.15}$. If the gadolinium compound is a stoichiometric one, then O_y and O_z are expected to be the values extrapolated from those of $NdCO_4$ and $EuCO_4$, that is, the values of × in Fig. 6. With these values the Cr–O bond length becomes 0.170 nm. Fig. 9(a) shows the model of $Cr_2O_7{}^{4-}$ ($(CrO_3$–O–$CrO_3)^{4-}$) cluster in $Gd_{0.9}CrO_{3.85}$, in which the centered oxygen atom, shared by

Table 5 Ionic radii of rare earth ions, r_{RE},[27] and the phase of rare earth chromates(v) reported by us and other authors. Symbols m, z, dz and × indicate monazite, normal zircon type, defect zircon type, and no single phase, respectively. References are indicated

Rare earth	$_{57}La$	$_{58}Ce$	$_{59}Pr$	$_{60}Nd$–$_{63}Eu$	$_{64}Gd$–$_{71}Lu$	$_{38}Y$
r_{RE}/nm	0.1160	0.1143	0.1126	0.1109–0.1079	0.1066–0.0977	0.1019
Our results	m[12]	× [12]	× [12]	z[12,13]	dz (present work)	dz (present work)
Other reports	m[1,6]	× [5,6]	× [2,6] or m[7]	z[3,5,11]	z[5,8–10]	z[4,8]

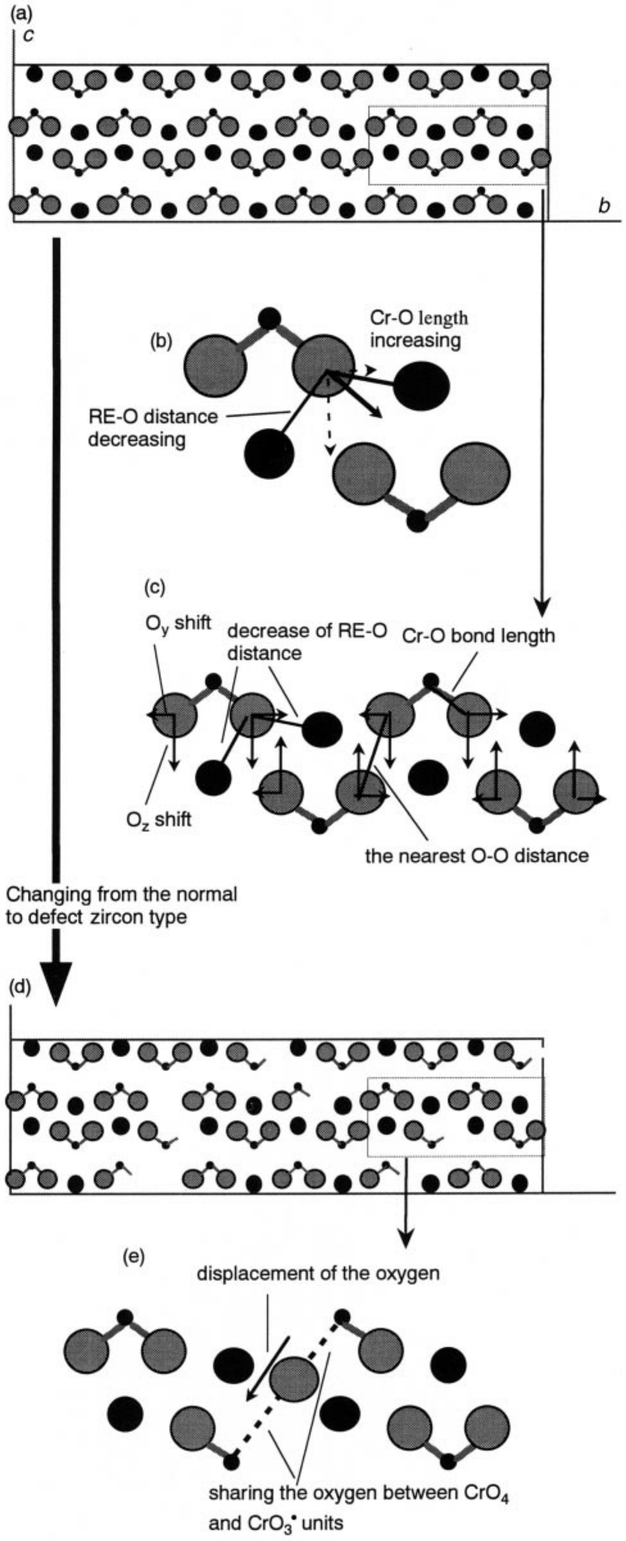

Fig. 7 (a) The 100 plane in the zircon type $EuCrO_4$, (b) the changes of 16h oxygen coordinates with decreasing r_{RE}, (c) the shift of the equivalent position of the 16h oxygen when the compound changes from normal to the defect zircon-type $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y), (d) the 100 plane in $Gd_{0.9}CrO_{3.85}$, and (e) displacement of the shared oxygen by $CrO_3^{\bullet}$ and CrO_4 units. Large dark, small black and large gray spheres show rare earth, chromium, and oxygen atoms, respectively.

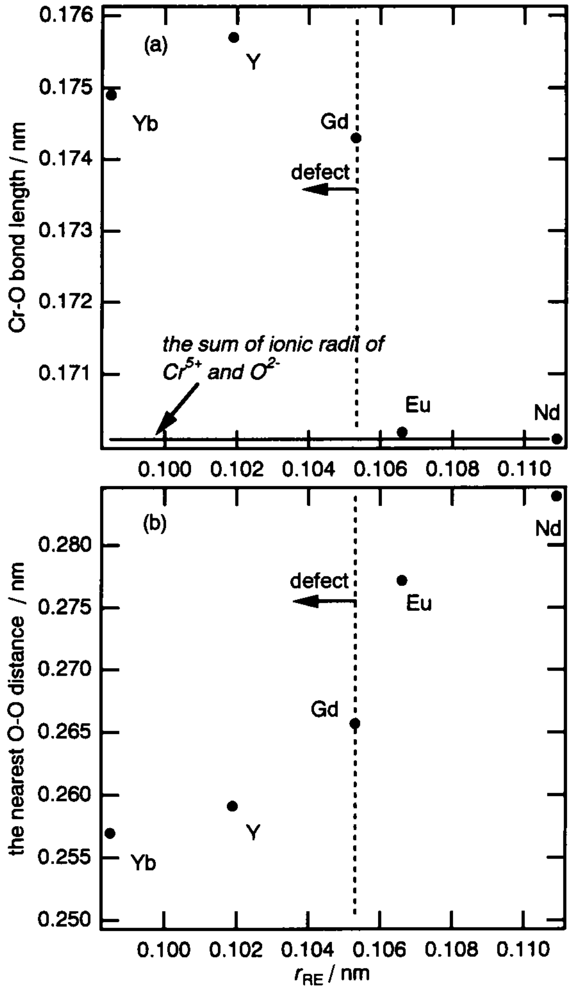

Fig. 8 Plot of (a) Cr–O bond length and (b) the nearest O–O distances between the neighboring CrO_4^{3-} units in the zircon-type rare earth chromates(v), as a function of ionic radius of RE^{III} ions, r_{RE}.

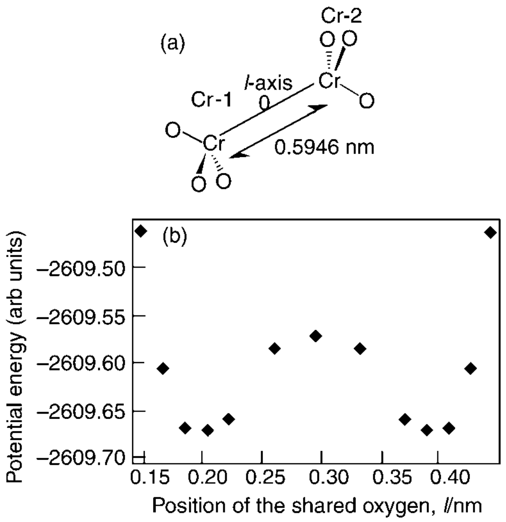

Fig. 9 (a) The $Cr_2O_7^{4-}$ cluster model and the *l*-axis, representing the position of the shared oxygen in $Gd_{0.9}CrO_{3.85}$. (b) The calculated potential energy of the $Cr_2O_7^{4-}$ cluster with displacement of the shared oxygen atom along the *l*-axis in (a). In (b), the *x*-axis value means the distance of the shared oxygen atom from Cr1.

$CrO_3^{\bullet}$ and CrO_4 units, displaces along *l*-axis between Cr1 and Cr2 atoms on the 200 plane and the distance of two Cr atoms is that determined by XRD. Here, it was assumed that only the centered oxygen can displace and other oxygen atoms occupy the sites which are expected from the coordinate change in Fig. 6 for the case of no abnormal elongation of Cr–O bonding, indicated by × symbols in Fig. 6. For this cluster model, the potential energy was calculated as a function of *l* as shown in Fig. 9(b), where the *l*-coordinate is the distance from Cr1 to the oxygen atom. It indicates that the oxygen in a Cr_2O_7 cluster should alternately belong to either of two Cr^V sites at the bottom of a typical W-type potential well. The bottom position is about 0.20 nm distant from each Cr atom, which is much longer than the Cr–O bond length in $EuCrO_4$ (Fig. 8). The result of calculation supports that the observed displacement of oxygen atoms by XRD measurements of $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) is due to the oxygen-sharing between CrO_4 and $CrO_3^{\bullet}$ units. All these results indicate that the defect structure of $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) is stabilized by the formation of a (CrO_3–O–CrO_3) unit mainly caused by the decrease of ionic radius of the rare earth atom.

Conclusions

Single phase zircon-type rare earth chromates containing Gd^{III}, Yb^{III} and Y^{III} ions were synthesized by pyrolysis of the precursors prepared from the mixed solutions of RE^{III} and Cr^{VI}, having a mole ratio of RE/Cr = 0.90/1.00. When RE/Cr $\geqslant$ 1.00/1.00, the pyrolysis products contained RE_2O_3, and when RE/Cr $\leqslant$ 0.85/1.00 they contained Cr_2O_3 as a secondary phase. The compositions of compounds were determined by chemical analyses with small standard deviations, indicating that the rare earth chromates are expressed as $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y). The ESR spectrum of $Y_{0.9}CrO_{3.85}$ coincided with Cr^V ions in solids with $g = 1.988$ and $\Delta H = 140$ mT, indicating that the valence state of chromium in these three compounds is pentavalent. The detailed structure was refined by the powder X-ray Rietveld method with good convergence. The density of $RE_{0.9}CrO_{3.85}$ (RE = Gd, Yb and Y) measured by pycnometry was in good agreement with the calculated density for the model that the structure is a defect zircon-type oxide with rare earth and oxygen vacancies, that is, $RE_{0.9}(CrO_4)_{0.85}(CrO_3^{\bullet})_{0.15}$. Structural analysis indicated that with increasing atomic number the Cr–O bond length abruptly increased at the boundary of Eu^{III} and Gd^{III} compounds. The value for Nd^{III} and Eu^{III} compounds was nearly the same with the sum of two crystal radii, Cr^V (0.049 nm, C.N. 4) and O^{2-} (0.121 nm, C.N. 2) but that for the compounds of Gd^{III}, Yb^{III} and Y^{III} was longer than 0.174 nm. From this and the property of $CrO_3^{\bullet}$ due to a dangling bond, the stability of the defect zircon-type structure can be attributed to the formation of the Cr_2O_7 (CrO_3–O–CrO_3) unit. The potential energy of the $Cr_2O_7^{4-}$ cluster calculated as a function of the distance of the centered oxygen atom from the Cr atom by *ab initio* MO methods revealed that it takes the minimum value when the centered oxygen is located *ca.* 0.22 nm from each Cr atom. This explains the elongation of the Cr–O bond length, on average, and the structural stabilization. By the present results, it can be concluded that the rare earth chromates(v), consisting of smaller RE^{III} ions than Eu^{III}, form the defect zircon-type structure, $RE_{0.9}CrO_{3.85}$, and not stoichiometric ones.

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