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Author(s)	Doi, Yoshihiro; Satou, Tatsuya; Hinatsu, Yukio
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Crystal structures and magnetic properties of lanthanide containing borates

Yoshihiro Doi, Tatsuya Satou, and Yukio Hinatsu

Division of Chemistry, Graduate School of Science, Hokkaido University
Sapporo 060-0810, Japan

Yoshihiro Doi

Division of Chemistry,
Graduate School of Science,
Hokkaido University,
Sapporo 060-0810, Japan.
TEL: +81-11-706-2715
FAX: +81-11-706-4931
E-mail: doi@sci.hokudai.ac.jp

Abstract

The synthesis, crystal structures and magnetic properties of $\text{LnM}(\text{BO}_3)_2$ ($\text{Ln} = \text{Y, Ho-Lu}$; $\text{M} = \text{Sc, Cr}$) were investigated. The $\text{LnCr}(\text{BO}_3)_2$ compounds crystallize in the dolomite-type structure with space group $R\bar{3}$, in which the Ln and Cr ions occupy two octahedral sites. From the result of structural analysis, it was found that there is an anti-site disorder between these two sites and its chemical formula is more exactly $\text{Ln}_{1-r}\text{Cr}_r[\text{Cr}_{1-r}\text{Ln}_r](\text{BO}_3)_2$. On the other hand, the $\text{LnSc}(\text{BO}_3)_2$ adopt the calcite-type structure with space group $R\bar{3}c$. The Ln and Sc ions randomly occupy an octahedral site and the chemical formula is represented as $(\text{Ln}_{0.5}\text{Sc}_{0.5})\text{BO}_3$. From the magnetic susceptibility and specific heat measurements, we found that all the $\text{LnCr}(\text{BO}_3)_2$ show an antiferromagnetic transition at 6.1–8.1 K. This transition is mainly due to the ordering of Cr^{3+} magnetic moments. Among the compounds with magnetic Ln^{3+} ions, only $\text{YbCr}(\text{BO}_3)_2$ shows an antiferromagnetic ordering of Ln^{3+} ion at 2.1 K.

Introduction

Recently, the physical properties of borate crystals containing lanthanide (Ln) ion attract great deal of interests. In particular, the $\text{LnM}_3(\text{BO}_3)_4$ ($\text{M} = \text{Al}, \text{Sc}, \text{Cr}, \text{Fe}, \text{Ga}$) with the huntite $\text{CaMg}_3(\text{CO}_3)_4$ related structures are extensively studied because of their interesting optical properties ($\text{M} = \text{Al}$) [1], the structural and magnetic phase transitions [2], and multiferroic properties [3] ($\text{M} = \text{Fe}$).

In order to explore further interesting materials, we focused our attention on the crystal structure and magnetic properties of the $\text{LnCr}(\text{BO}_3)_2$ borates. They were first synthesized by Vicat and Aléonard in 1968 and the crystal structure was determined to be isostructural to the mineral dolomite $\text{CaMg}(\text{CO}_3)_2$ [4, 5]. In that structure, the Ln and Cr ions individually occupy two octahedral sites, and LnO_6 and MO_6 octahedra alternatively connect to each other by sharing corner oxygen. Such a structural feature has been of great interest in the sight of the magnetism because the existence of Ln–O–Cr superexchange pathway may bring about anomalous magnetic properties due to the magnetic interaction between f and d electrons which has been reported for ordered double perovskites A_2LnMO_6 ($\text{A} = \text{alkali earth}$; $\text{M} = 4\text{d}, 5\text{d}$ transition metal) [6–10]. Nevertheless, the physical properties of $\text{LnCr}(\text{BO}_3)_2$ are unknown although long time has passed since first synthesis to our best knowledge.

In this paper, we will report the detailed crystal structure for $\text{LnCr}(\text{BO}_3)_2$, and reveal their magnetic properties by the magnetic susceptibility and specific heat measurements at low

temperatures. In addition, we also synthesized the scandium analogues $\text{LnSc}(\text{BO}_3)_2$ to make a comparative study in regard to the crystal structure and the magnetic behavior of lanthanide ion.

Experimental

Sample preparation

Polycrystalline samples of $\text{LnM}(\text{BO}_3)_2$ ($\text{Ln} = \text{Y, Ho-Lu}$; $\text{M} = \text{Sc, Cr}$) were prepared by the standard solid-state reaction. As starting materials, Ln_2O_3 , M_2O_3 , H_3BO_3 were used. These starting materials were weighed in the molar ratio 1 : 1 : 5.2, in which a 30 % excess of H_3BO_3 was added to compensate for the volatilization loss, and ground intimately in an agate mortar. The mixtures were pressed into pellets and enclosed in a platinum tube. Then it was heated slowly up to 1100 °C (1 °C/min) in a flow of N_2 gas, and this temperature was kept for 6 h. This heating procedure is repeated 2–5 times.

Powder x-ray diffraction measurements

Powder X-ray diffraction (XRD) measurements were performed at room temperature using a Rigaku MultiFlex diffractometer with a $\text{Cu-K}\alpha$ X-ray radiation source equipped with a curved graphite-monochromator. The data were collected by step-scanning in the angle range of $10^\circ \leq 2\theta \leq 120^\circ$ at a step size 0.02°. The XRD data were analyzed by the Rietveld method using the program RIETAN-FP [11] and the crystal structure was drawn by using the VESTA program [12].

Magnetic susceptibility and specific heat measurements

The temperature dependence of the magnetic susceptibilities was measured with a SQUID magnetometer (Quantum Design, MPMS-5S). The measurements were performed under both zero-field-cooled (ZFC) and field-cooled (FC) conditions over the temperature range 1.8–300 K in an applied magnetic field of 0.1 T.

The specific heat measurements were performed using a relaxation technique with a commercial physical property measurement system (Quantum Design, PPMS) in the temperature range of 1.8–300 K. The pelletized sample was mounted on a thin alumina plate with Apiezon N grease for better thermal contact.

Results and discussion

Crystal structures

Polycrystalline samples of $\text{LnCr}(\text{BO}_3)_2$ ($\text{Ln} = \text{Y}, \text{Ho-Lu}$) were successfully prepared. They contain small amount (2–5 %) of decomposed products (Cr_2O_3 and LnBO_3). All the XRD profiles were indexed on a rhombohedral unit cell, and analyzed by the Rietveld method. As the starting model of analysis, we firstly used the structural data for $\text{LnCr}(\text{BO}_3)_2$ in an earlier work [5] with the dolomite-type structure (space group $R\bar{3}$) in which the Ln and Cr ions occupy individual

crystallographic sites; however the calculated profiles showed a poor fit to the observed ones because of the different ratios of peak intensity. In order to improve the fitting, we analyzed the data by assuming the anti-site disorder between Ln (3a) and Cr (3b) sites. Such a disorder is found in the dolomite $\text{CaMg}(\text{CO}_3)_2$ [13]. The calculated profiles give a good agreement with observed ones as shown in Fig. 1(a), and the refined structural parameters and reliability factors are summarized in Table 1.

On the other hand, we have also prepared scandium analogues $\text{LnSc}(\text{BO}_3)_2$ ($\text{Ln} = \text{Y}, \text{Ho-Lu}$). The XRD profile for $\text{Ln} = \text{Tm}$ compound is plotted in Fig. 1(b). All these compounds have a rhombohedral unit cell with the calcite CaCO_3 structure (space group $R\bar{3}c$) [14]. In fact, it is known that the ScBO_3 [15] and LnBO_3 with smaller Ln ions ($\text{Ln} = \text{Yb}$ and Lu) [16, 17] adopt this structural type; thus the crystal structure of $\text{LnSc}(\text{BO}_3)_2$ can be regarded as a solid-solution $(\text{Ln}_{0.5}\text{Sc}_{0.5})\text{BO}_3$. Although the LnBO_3 for larger Ln ions adopt other crystal structures [18, 19], the small average radius, $(R_{\text{Ln}^{3+}} + R_{\text{Sc}^{3+}})/2 = 0.804\text{--}0.823 \text{ \AA}$ for $\text{Ln} = \text{Y}, \text{Ho-Lu}$ from the Shannon's ionic radius [Shannon], may stabilize the calcite structure. The calculated profile by using the calcite model is shown in Fig. 1(b), and refined structural parameters and reliability factors are listed in Table 2.

The schematic crystal structures of $\text{LnCr}(\text{BO}_3)_2$ and $\text{LnSc}(\text{BO}_3)_2$ are illustrated in Fig. 2, and some selected bond lengths and angles are listed in Table 3. In both structures, the Ln and M ions occupy the octahedral sites. The LnO_6 and MO_6 octahedra form a three dimensional network by sharing corner-oxygen ions and the BO_3 triangle shares oxygen ions of octahedra. Both structures are

similar to each other except for the difference in the partially or fully disordered arrangements of octahedral sites. For the $\text{LnCr}(\text{BO}_3)_2$ compounds, when the occupancy of Cr ions at the $3a$ site is r , the chemical formula is represented as $\text{Ln}_{1-r}\text{Cr}_r[\text{Cr}_{1-r}\text{Ln}_r](\text{BO}_3)_2$ ($0 < r < 0.5$). Therefore, they have two octahedral sites, i.e., the (Ln,Cr)(1) site with a longer bond length to oxygen ion and the (Ln,Cr)(2) site with a shorter bond length.

The degree of disorder appears in the peak intensity of $\{ h\bar{h}il \}$ ($h + l = 3n$) reflections shown in Fig. 1(a) because their structure factors contain a term: $3f_{3a} - 3f_{3b} = 3(1 - 2r)(f_{\text{Ln}^{3+}} - f_{\text{Cr}^{3+}})$ in which f means the scattering factor of a site or ion. Such peaks become strongest for the case of a fully ordered arrangement ($r = 0.0$) and negligibly weak for disordered one ($r = 0.5$). In the case of the $\text{LnSc}(\text{BO}_3)_2$, these reflections are forbidden from the $R\bar{3}c$ symmetry, and the calculation of r value assuming the $R\bar{3}$ model also supports the fully disordered arrangement ($r = 0.50 \pm 0.02$). Figure 3 shows the variation of the r value against the difference of ionic radius, $\Delta R = R_{\text{Ln}^{3+}} - R_{\text{M}^{3+}}$, and for comparison, a constant value $r = 0.5$ for $\text{LnSc}(\text{BO}_3)_2$ is also plotted. For $\text{LnCr}(\text{BO}_3)_2$, the r decreases linearly with increasing ΔR and approaches to zero. On the other hand, the data of fully disordered $\text{LnSc}(\text{BO}_3)_2$ are in smaller ΔR region. These results indicate that as the difference in ionic radius between Ln and M ions becomes larger, these compounds adopt more ordered arrangement.

The lattice parameters of $\text{LnCr}(\text{BO}_3)_2$ and $\text{LnSc}(\text{BO}_3)_2$ are plotted in Fig. 4 as a function of the ionic radius $R_{\text{Ln}^{3+}}$. In both series, the lattice parameters a and c increase with $R_{\text{Ln}^{3+}}$. However, the increment of a from Ln = Lu to Ho ($0.016 \text{ \AA}$ for M = Cr and $0.019 \text{ \AA}$ for Sc) is much smaller than

that of c (0.148 Å for Cr and 0.156 Å for Sc). The tendency shows a good agreement with the result in the $\text{LnCr}(\text{BO}_3)_2$ and other dolomite-type borates [4, 5].

Magnetic properties

$\text{LnSc}(\text{BO}_3)_2$ (Ln = Ho–Yb)

The temperature dependence of the inverse magnetic susceptibility (χ_M^{-1}) for $\text{LnSc}(\text{BO}_3)_2$ (Ln = Ho–Yb) is plotted in Figs. 5(a) and (b). These compounds are paramagnetic in the whole experimental temperature range. The data were fitted with the Curie-Weiss law in the temperature range of 100–300 K, and the effective magnetic moments (μ_{eff}) and Weiss constants (θ) were calculated. These parameters are listed in Table 4. The effective magnetic moments are consistent with the free-ion values of trivalent Ln ions. In these compounds, no magnetic transition is observed down to 1.8 K, which is due to the magnetic dilution (50 %) by diamagnetic Sc^{3+} ion.

The absolute values of θ are abnormally large compared with the relationship of $|\theta| \sim T_N$ in the molecular field theory. This result is derived from the crystal field splitting of Ln^{3+} ions, which is found in a deviation from the linearity of χ_M^{-1} vs T plot. For the Yb^{3+} ion, if we ignore the trigonal distortion of YbO_6 octahedron in $\text{YbSc}(\text{BO}_3)_2$, the $^2F_{7/2}$ ground multiplet is split into two doublets Γ_6 and Γ_7 and a quartet Γ_8 in the octahedral crystal field [21]. In this case, the magnetic susceptibility is represented as the following equation [22]:

$$\chi_M(\text{Yb}^{3+}) = \frac{N_A g_J^2 \mu_B^2 J(J+1)}{3k_B T} \times \frac{98 + 260e^{-\beta} + 162e^{-\alpha} + 432(e^{-\beta} - e^{-\alpha})/(\alpha - \beta) + 560(1 - e^{-\beta})/\beta}{378(1 + 2e^{-\beta} + e^{-\alpha})} \quad (1)$$

where $\alpha = (E_{\Gamma 7} - E_{\Gamma 6})/k_B T$ and $\beta = (E_{\Gamma 8} - E_{\Gamma 6})/k_B T$. The fitting curve by Eq. (1) between 10 and 300 K is shown in Fig. 5(b) and it shows a good agreement with the experimental data. We obtained the energy differences $E_{\Gamma 8} - E_{\Gamma 6} = 562(8)$ K and $E_{\Gamma 7} - E_{\Gamma 6} = 1515(97)$ K, and the effective magnetic moment of $4.50(1) \mu_B$, which are comparable with those for the perovskite-type oxides containing the Yb^{3+} ion at the octahedral site [23, 24].

LnCr(BO₃)₂ (Ln = Y, Lu)

Figure 6(a) shows the data of inverse magnetic susceptibility as a function of temperature and the fitting curves by the Curie-Weiss law for $\text{LnCr(BO}_3)_2$ (Ln = Y, Lu). Their effective magnetic moments and Weiss constants are listed in Table 4. In both compounds, only the Cr ion is magnetic and the others are diamagnetic. Their μ_{eff} values are close to the free-ion value of Cr^{3+} ($S = 3/2$) ion. The negative Weiss constants mean that the predominant magnetic interaction between Cr ions is antiferromagnetic.

The magnetic susceptibilities vs. temperature curves at low temperature region for $\text{YCr(BO}_3)_2$ and $\text{LuCr(BO}_3)_2$ are plotted in Figs. 7 and 8, respectively. In both compounds, a cusp is observed at 8.1 K (Y) or 6.5 K (Lu). In addition, the temperature dependence of specific heat (middle plot of the

figures) also shows a λ -type anomaly at the same temperature. These results show that the antiferromagnetic transition occurs in these compounds. From the specific heat data, it is observed that the $\text{YCr}(\text{BO}_3)_2$ shows a sharp λ -type anomaly while the $\text{LuCr}(\text{BO}_3)_2$ shows a broader one. This difference may be related to the degree of anti-site disorder between Ln and Cr ions (Lu: 15.2 %; Y: 3.0 %).

To obtain further information about the magnetic transition, the temperature dependence of magnetic entropy (S_{mag}) was calculated by $S_{\text{mag}} = \int_0^T (C_{\text{mag}}/T)dT$, in which the magnetic specific heat (C_{mag}) was estimated by subtracting the lattice and electronic specific heat from the experimental specific heat of $\text{LnCr}(\text{BO}_3)_2$. For this purpose, we used the specific heat of $\text{YSc}(\text{BO}_3)_2$ or $\text{LuSc}(\text{BO}_3)_2$. The magnetic specific heat below 1.8 K was extrapolated by the relation $C_{\text{mag}} \propto T^3$ from the spin-wave model for an antiferromagnet [25]. The C_{mag}/T and S_{mag} are also plotted in Figs. 7 and 8. The S_{mag} values at 20 K are 9.5 J/mol K for $\text{YCr}(\text{BO}_3)_2$ and 10.0 J/mol K for $\text{LuCr}(\text{BO}_3)_2$, and gradually increase with temperature. It is considered that they reaches a theoretical value $R \ln (2S + 1) = 11.53$ J/mol K for $S = 3/2$ ion. Thus, the observed magnetic transition is due to the long-range antiferromagnetic ordering of Cr^{3+} ($3d^3$) moments.

$\text{LnCr}(\text{BO}_3)_2$ (Ln = Ho–Yb)

The temperature dependence of inverse magnetic susceptibility for $\text{LnCr}(\text{BO}_3)_2$ (Ln = Ho–Yb) is plotted in Fig. 6(b). Their effective magnetic moments and Weiss constants are summarized in

Table 4. The determined μ_{eff} values are in good agreement with the calculated ones from $\mu_{\text{cal}} = \sqrt{\mu_{\text{Cr}^{3+}}^2 + \mu_{\text{Ln}^{3+}}^2}$. The negative Weiss constants indicate the existence of antiferromagnetic interaction except for the θ of $\text{YbCr}(\text{BO}_3)_2$ which is strongly affected by the crystal field splitting of Yb^{3+} ion as with the case of $\text{YbSc}(\text{BO}_3)_2$.

Figures 9–12 represent the temperature dependences of magnetic susceptibility and specific heat for $\text{LnCr}(\text{BO}_3)_2$ ($\text{Ln} = \text{Ho–Yb}$). All of them show an antiferromagnetic transition at 6.1–7.9 K. The magnetic specific heat and magnetic entropy are estimated by the same way as the case for $\text{LuCr}(\text{BO}_3)_2$, and they are shown in bottom graphs of each figure. The S_{mag} values at 20 K are calculated to be 18.8 (for $\text{Ln} = \text{Ho}$ compound), 14.1 (Er), 9.4 (Tm), and 12.3 (Yb) J/mol K. The S_{mag} value for Tm compound is close to those for Y and Lu ones. This result indicates that the Tm^{3+} contribution to the magnetic entropy S_{mag} is negligibly small. In fact the temperature independent behavior of χ_M^{-1} at low temperatures for the related Sc compound $\text{TmSc}(\text{BO}_3)_2$ (see inset of Fig. 5(a)) means that the Tm^{3+} ion is in a singlet (non-magnetic) ground state. On the other hand, the S_{mag} values for $\text{Ln} = \text{Ho, Er, and Yb}$ compounds show both the Ln^{3+} and Cr^{3+} ions contribute to the magnetic entropy of the compounds. However, for the Ho and Er compounds, the magnetic susceptibility and specific heat do not show well-marked anomaly derived from the Ln magnetic ordering below T_N . The Schottky anomaly due to the discrete Zeeman levels of Ln^{3+} ion by the internal magnetic field may contribute to the observed S_{mag} .

In the case of $\text{YbCr}(\text{BO}_3)_2$, an additional magnetic anomaly of specific heat is observed at 2.1 K

as shown in Fig. 12. The variation of S_{mag} for this transition at 4 K, $\Delta S_{\text{mag}} = S_{\text{mag}}(\text{Ln} = \text{Yb}) - S_{\text{mag}}(\text{Lu})$, is approximately 3.2 J/mol K. This result indicates that the magnetic moments of Yb also order although the value is somewhat smaller than $R \ln 2 = 5.76$ J/mol K expected from the ground doublet of Yb^{3+} ion. In the temperature dependence of the magnetic susceptibility, a rapid increase is observed below ~ 2.5 K. The data collected in a small applied field (0.005 T) obviously shows a magnetic anomaly with the divergence between ZFC and FC susceptibilities. These results indicate the existence of a ferromagnetic moment. However, its magnitude ($\sim 0.04 \mu_B/\text{mol}$) is very small as a ferromagnetic ordering of Yb^{3+} ion. Therefore, the magnetic transition found at 2.1 K is essentially antiferromagnetic, and the small ferromagnetic moment may be caused by the spin canting.

The Néel temperature for all the $\text{LnCr}(\text{BO}_3)_2$ is summarized in Table 4. The difference in T_N between the compounds containing magnetic Ln (Ho, Er, and Yb) ions and those containing nonmagnetic ions (Y, (Tm), and Lu) is much smaller than expected, in spite of the existence of Ln–O–Cr superexchange pathway in this crystal structure. This result indicates that the observed transition is mainly due to the antiferromagnetic ordering of Cr^{3+} ions. One reason for weak magnetic interaction via Ln–O–Cr is that its angle $\sim 124^\circ$ is highly deviated from 180° (or 90°) for the ideal superexchange interaction, and such a deviation often weakens the magnetic interaction as observed in double perovskites A_2LnRuO_6 (A = Ca, Sr, and Ba) [10]. In order to clarify the magnetic ordering behavior of Ln ions, the determination of magnetic structure by the neutron diffraction is needed.

Summary

We investigated the synthesis, crystal structures and magnetic properties of lanthanide-metal borates $\text{LnM}(\text{BO}_3)_2$ ($\text{Ln} = \text{Y, Ho-Lu}$; $\text{M} = \text{Sc, Cr}$). They adopt two related structures: the dolomite-type structure with anti-site disorder in octahedral sites for $\text{M} = \text{Cr}$ and the calcite-type structure for $\text{M} = \text{Sc}$. The marked difference between them is the partially or fully disordered arrangements of octahedral sites, and there is a tendency that a larger difference in ionic radius between Ln and M ions brings about more ordered arrangement.

From the results of the magnetic measurements, it is found that the $\text{LnSc}(\text{BO}_3)_2$ are paramagnetic down to 1.8 K and $\text{LnCr}(\text{BO}_3)_2$ show an antiferromagnetic transition at 6.1–8.1 K. This magnetic transition is mainly due to the antiferromagnetic ordering of Cr^{3+} ions. The $\text{YbCr}(\text{BO}_3)_2$ shows another antiferromagnetic transition at 2.1 K due to the magnetic ordering of Yb^{3+} ion.

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Figure captions

Fig. 1 Powder x-ray diffraction profiles for $\text{TmM}(\text{BO}_3)_2$ ($\text{M} = \text{Cr}$ and Sc). The calculated and observed diffraction profiles are shown on the top as a solid line and cross markers, respectively. The red vertical markers show positions calculated from Bragg reflections. The bottom trace is a plot of the difference between the calculated and observed intensities. In (a), middle (purple) and bottom (dark green) vertical marks mean Bragg reflections due to the impurity phases Cr_2O_3 (2.6 wt%) and TmBO_3 (2.9 wt%), respectively.

Fig. 2 Schematic crystal structures of (a) $\text{LnCr}(\text{BO}_3)_2$ and (b) $\text{LnSc}(\text{BO}_3)_2$. The $\text{LnCr}(\text{BO}_3)_2$ has a dolomite-type structure with anti-site disorder between two octahedral sites, i.e., $\text{Ln}_{1-r}\text{Cr}_r[\text{Cr}_{1-r}\text{Ln}_r](\text{BO}_3)_2$. The $\text{LnSc}(\text{BO}_3)_2$ adopts a calcite-type structure, more properly, its chemical formula is $(\text{Ln}_{0.5}\text{Sc}_{0.5})\text{BO}_3$.

Fig. 3 Variation of r value in partially disordered dolomite-type $\text{Ln}_{1-r}\text{Cr}_r[\text{Cr}_{1-r}\text{Ln}_r](\text{BO}_3)_2$ against the difference of 6-coordinate ionic radius, $\Delta R = R_{\text{Ln}^{3+}} - R_{\text{M}^{3+}}$. For comparison, a constant value $r = 0.5$ for calcite-type $(\text{Ln}_{0.5}\text{Sc}_{0.5})\text{BO}_3$ is also plotted.

Fig. 4 Variation of lattice parameters with the ionic radius of Ln ion for $\text{LnM}(\text{BO}_3)_2$ ($\text{M} = \text{Cr}$ and Sc).

Fig. 5 Temperature dependence of the inverse magnetic susceptibility for $\text{LnSc}(\text{BO}_3)_2$ ($\text{Ln} = \text{Ho-Lu}$). The red solid lines ($T = 100\text{--}300$ K) represent fitting curves by the Curie-Weiss law. In (b), a blue line ($T = 10\text{--}300$ K) is a fitting curve to Eq. (1).

Fig. 6 Temperature dependence of the inverse magnetic susceptibility for $\text{LnCr(BO}_3)_2$ ($\text{Ln} = \text{Ho-Lu}$). The red solid lines represent fitting curves by the Curie-Weiss law.

Fig. 7 Temperature dependence of the magnetic susceptibility, specific heat, magnetic specific heat, and magnetic entropy for $\text{YCr(BO}_3)_2$.

Fig. 8 Temperature dependence of the magnetic susceptibility, specific heat, magnetic specific heat, and magnetic entropy for $\text{LuCr(BO}_3)_2$.

Fig. 9 Temperature dependence of the magnetic susceptibility, specific heat, magnetic specific heat, and magnetic entropy for $\text{HoCr(BO}_3)_2$.

Fig. 10 Temperature dependence of the magnetic susceptibility, specific heat, magnetic specific heat, and magnetic entropy for $\text{ErCr(BO}_3)_2$.

Fig. 11 Temperature dependence of the magnetic susceptibility, specific heat, magnetic specific heat, and magnetic entropy for $\text{TmCr(BO}_3)_2$.

Fig. 12 Temperature dependence of the magnetic susceptibility, specific heat, magnetic specific heat, and magnetic entropy for $\text{LuCr(BO}_3)_2$. Inset shows the magnetic susceptibilities measured in an applied magnetic field of 0.005 T.

Table 1 Structural parameters and reliability factors for $\text{LnCr}(\text{BO}_3)_2$.

	Y	Ho	Er	Tm	Yb	Lu
$a / \text{\AA}$	4.7621(2)	4.7641(2)	4.7579(2)	4.7506(3)	4.7502(4)	4.7477(4)
$c / \text{\AA}$	15.5063(6)	15.5171(7)	15.4705(6)	15.4615(8)	15.4289(12)	15.3696(11)
$V / \text{\AA}^3$	304.53(2)	305.00(3)	303.29(2)	302.20(3)	301.50(4)	300.03(4)
(Ln, Cr)(1)						
r^{*1}	0.030(3)	0.041(2)	0.040(1)	0.063(1)	0.126(1)	0.152(1)
$B / \text{\AA}^2$	0.36(2)	0.51(2)	0.38(2)	0.30(2)	0.31(2)	0.66(2)
B						
z	0.7577(5)	0.7580(5)	0.7574(5)	0.7577(7)	0.7548(7)	0.7539(7)
O						
x	0.3055(5)	0.3046(6)	0.3046(5)	0.3044(5)	0.3032(6)	0.3034(6)
y	0.0307(6)	0.0301(7)	0.0286(6)	0.0273(6)	0.0212(7)	0.0182(7)
z	0.7569(2)	0.7557(2)	0.7568(2)	0.7570(2)	0.7547(2)	0.7542(2)
$B / \text{\AA}^2$	0.39(5)	0.62(6)	0.41(6)	0.34(6)	0.64(6)	1.05(12)
$R_{\text{wp}} / \%$	10.04	10.96	8.66	6.57	9.11	9.02
$R_{\text{p}} / \%$	7.08	7.67	6.19	4.86	6.42	6.43
$R_{\text{B}} / \%$	1.71	1.61	1.09	1.01	1.29	1.48
$R_{\text{e}} / \%$	6.78	8.00	5.60	4.81	6.29	6.62

Note. Dolomite-type structure with space group $R\bar{3}$; (Ln, Cr)(1): $3a(0,0,0)$, (Ln, Cr)(2): $3b(0,0,1/2)$, B: $6c(0,0,z)$, O: $18f(x,y,z)$; $B_{(\text{Ln,Cr})(2)} = B_{(\text{Ln,Cr})(1)}$, $B_{\text{B}} = 0.3 \text{\AA}^2$.

^{*1} Occupancy of Cr ion at $3a$ site: r in the $\text{Ln}_{1-r}\text{Cr}_r[\text{Cr}_{1-r}\text{Ln}_r](\text{BO}_3)_2$.

Table 2 Structural parameters and reliability factors for $\text{LnSc}(\text{BO}_3)_2$.

	Y	Ho	Er	Tm	Yb	Lu
$a / \text{\AA}$	4.8581(4)	4.8593(6)	4.8532(4)	4.8449(4)	4.8403(4)	4.8402(5)
$c / \text{\AA}$	15.9671(10)	15.9808(16)	15.9186(10)	15.8979(12)	15.8339(11)	15.8245(13)
$V / \text{\AA}^3$	326.35(4)	326.79(6)	324.70(4)	323.17(4)	321.26(4)	321.06(5)
$\text{Ln}_{0.5}\text{Sc}_{0.5}$						
$B / \text{\AA}^2$	0.70(3)	0.77(3)	0.60(3)	0.59(3)	0.36(2)	0.57(2)
O						
x	0.7150(4)	0.7165(5)	0.7149(5)	0.7136(5)	0.7146(4)	0.7166(5)
$B / \text{\AA}^2$	0.79(5)	0.55(6)	0.57(6)	0.66(7)	0.30(5)	0.40(6)
$R_{\text{wp}} / \%$	12.06	11.63	10.26	8.24	8.40	10.77
$R_{\text{p}} / \%$	8.85	8.52	7.73	6.31	6.18	7.98
$R_{\text{B}} / \%$	2.86	3.62	3.78	2.50	1.65	2.91
$R_{\text{e}} / \%$	9.48	9.48	8.15	6.99	5.95	8.40

Note. Calcite-type structure with space group $R\bar{3}c$; the accurate chemical formula: $(\text{Ln}_{0.5}\text{Sc}_{0.5})\text{BO}_3$; $\text{Ln}_{0.5}\text{Sc}_{0.5}$: $6b(0,0,0)$, B: $6a(0,0,1/4)$, O: $18e(x,0,1/4)$; $B_{\text{B}} = 0.3 \text{\AA}^2$.

Table 3 Bond lengths and angles of $\text{LnSc}(\text{BO}_3)_2$ and $\text{LnCr}(\text{BO}_3)_2$.

		Y	Ho	Er	Tm	Yb	Lu
$\text{LnSc}(\text{BO}_3)_2$.							
$(\text{Ln}_{0.5}\text{Sc}_{0.5})\text{--O} / \text{\AA}$	$\times 6$	2.197(1)	2.202(1)	2.193(1)	2.187(1)	2.185(1)	2.189(1)
$\text{B--O} / \text{\AA}$	$\times 3$	1.385(2)	1.378(2)	1.384(2)	1.387(3)	1.382(2)	1.372(3)
$\text{O--}(\text{Ln}_{0.5}\text{Sc}_{0.5})\text{--O} / ^\circ$	$\times 6$	87.1(3)	87.2(3)	87.2(3)	87.1(3)	87.3(3)	87.4(3)
$(\text{Ln}_{0.5}\text{Sc}_{0.5})\text{--O--}(\text{Ln}_{0.5}\text{Sc}_{0.5}) / ^\circ$	$\times 6$	123.2(9)	122.9(10)	123.2(11)	123.5(11)	123.2(9)	122.8(12)
$\text{LnCr}(\text{BO}_3)_2$							
$(\text{Ln,Cr})(1)\text{--O} / \text{\AA}$	$\times 6$	2.283(3)	2.272(3)	2.272(3)	2.267(3)	2.223(3)	2.203(3)
$(\text{Ln,Cr})(2)\text{--O} / \text{\AA}$	$\times 6$	1.990(3)	2.006(3)	1.994(3)	1.992(3)	2.023(3)	2.028(3)
$\text{B--O} / \text{\AA}$	$\times 3$	1.388(2)	1.386(2)	1.386(2)	1.386(2)	1.393(2)	1.399(2)
$\text{O--}(\text{Ln,Cr})(1)\text{--O} / ^\circ$	$\times 6$	86.3(9)	86.9(10)	86.3(9)	86.0(9)	86.6(11)	86.6(12)
$\text{O--}(\text{Ln,Cr})(2)\text{--O} / ^\circ$	$\times 6$	88.2(11)	87.6(11)	88.3(10)	88.5(10)	87.7(12)	87.7(13)
$(\text{Ln,Cr})(1)\text{--O--}(\text{Ln,Cr})(2) / ^\circ$	$\times 6$	123.9(8)	123.8(11)	123.9(10)	124.1(10)	124.5(11)	124.9(13)

Table 4 Magnetic properties for $\text{LnSc}(\text{BO}_3)_2$ and $\text{LnCr}(\text{BO}_3)_2$.

	Y	Ho	Er	Tm	Yb	Lu
$\text{LnSc}(\text{BO}_3)_2$						
Magnetic properties ^{*1}	DM	PM	PM	PM	PM	DM
$\mu_{\text{eff}} / \mu_{\text{B}}$		10.51(1)	9.50(1)	7.65(1)	4.45(1)	
$\mu_{\text{Ln}^{3+}} / \mu_{\text{B}}$ ^{*2}		10.58	9.59	7.55	4.54	
θ / K		-12.9(3)	-22.7(5)	-28.2(2)	-101.6(8)	
$\text{LnCr}(\text{BO}_3)_2$						
Magnetic properties ^{*1}	AF	AF	AF	AF	AF	AF
$\mu_{\text{eff}} / \mu_{\text{B}}$	3.58(1)	10.85(1)	10.15(1)	8.06(1)	5.66(2)	3.38(1)
$\mu_{\text{cal}} / \mu_{\text{B}}$ ^{*3}	3.87	11.27	10.34	8.49	5.97	3.87
θ / K	-3.3(8)	-11.0(4)	-9.4(2)	-21.7(3)	-47(2)	-6.9(7)
T_{N} / K	8.1	7.9	7.7	7.2	6.1, 2.1	6.5

^{*1} DM: diamagnetic, PM: paramagnetic, AF: antiferromagnetic.

^{*2} Theoretical values.

^{*3} Calculated effective magnetic moment from $\sqrt{\mu_{\text{Cr}^{3+}}^2 + \mu_{\text{Ln}^{3+}}^2}$, where $\mu_{\text{Cr}^{3+}} = 3.87 \mu_{\text{B}}$.

Figure 1

Figure 2

Figure 3

Figure 4

(a)

(b)

Figure 5

(a)

(b)

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11