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Crystal Structures of the Europium and Yttrium Hydroxychromate: $Eu(OH)(CrO_4)$ and $Y(OH)(CrO_4)$. Structural evolution as a function of the Ln^{3+} ionic radius.

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Abstract: The $Eu(OH)(CrO_4)$ and $Y(OH)(CrO_4)$ compounds were obtained under hydrothermal conditions and characterized by single crystal X-ray diffraction analysis. They are isostructural and crystallize in the monoclinic system, space group $P2_1/n$ (no. 14) with lattice parameters a = 8.278(1) Å, b = 11.400(2) Å, c = 8.393(1) Å, β = 93.76(2)°, V = 790.3(2) Å^3, Z = 4, d = 4.79 g.cm^{-3} for Eu(OH)(CrO4) and a = 8.151(1) Å, b = 11.362(2) Å, c = 8.285(1) Å, β = 94.23(1)°, V = 765.2(2) Å^3, Z = 4, d = 3.85 g.cm^{-3} for $Y(OH)(CrO_4)$. The $[EuO_8]$ polyhedra form infinite double chains along the a direction which are connected by common edges and corners. These double chains are related together in the two other directions *via* the $[CrO_4]^{2-}$ tetrahedra to form a three-dimensional network in which channels appear parallel to the [100] direction. We examine the structural evolution, as a function of the Ln^{3+} ionic radius, in the series $Ln(OH)(CrO_4)$ compounds (with Ln = Nd, Eu, Gd, Tb, Er, Yb) and $Y(OH)(CrO_4)$. To determine the best coordination number of each lanthanide and yttrium ions, different calculations of bond valence sum have been realized.

Keywords: Bond Valence Sum; Chromate; Crystal structure; Europium; Yttrium

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The research of materials for quadratic nonlinear optics (NLO) is bound by many severe requirements and the first one is that the crystal structure must be acentric [1]. The coordination of acentric ligands to cations favours the formation of non-centrosymmetric structures. Among these ligands, we can mention the iodate ion IO_3^- with a lone pair of electrons on iodine and the chromate ion CrO_4^{2-}, having a trigonal pyramidal and tetrahedral geometry, respectively. The first one leads us to synthesize many compounds some of which crystallizing in polar space groups [2-4]. The second one also leads to materials crystallizing with acentric structures such as $RbLiCrO_4$, $KTb(CrO_4)_2$ and $AgBi(CrO_4)_2$ [5-7]. Here, we report on the crystal structure of $Eu(OH)(CrO_4)$ and $Y(OH)(CrO_4)$ obtained by hydrothermal procedure. Then we examine the structural evolution, as a function of the Ln^{3+} ionic radius along the series $Ln(OH)(CrO_4)$ for which crystal structures have been characterized in this paper (Eu and Y) or previously (Nd, Gd, Tb, Er and Yb) [8-11]. Bueno *et al.* had already highlight the existence of $Y(OH)(CrO_4)$ and $Ln(OH)(CrO_4)$ (with Ln = Dy, Yb, Lu) isotypic phases based on the analogy of the diffraction patterns with the one of $Er(OH)(CrO_4)$ [8]. Only unit cell parameters had been given.

Results and discussion

The $Eu(OH)(CrO_4)$ and $Y(OH)(CrO_4)$ are isostructural with other $Ln(OH)(CrO_4)$ compounds (Ln = Nd, Gd, Tb, Er and Yb) [8-11] and crystallize in the monoclinic space group $P2_1/n$. The following description is exemplified for the $Eu(OH)(CrO_4)$ compound, as structural features are similar in both compounds with only slight variations in bond length and angles. Asymmetric unit is built up by two europium ions, two chromate groups and two hydroxyl groups leading to a three-dimensional network. Each europium atom is surrounded by seven oxygen atoms (provided

by three hydroxyl functions and four chromate groups) with bond lengths ranging from 2.321(8) Å to 2.446(6) Å for Eu1 and from 2.349(7) Å to 2.481(6) Å for Eu2. A longer Eu-O distance with a fifth chromate group (2.640(7) Å and 2.572(7) Å for Eu1 and Eu2 respectively) (Table 1) is observed. The gap between the seventh and the eighth Eu-O distance is around 0.2 and 0.1 Å for Eu1 and Eu2 respectively. Taking into account only the seven shorter bond lengths, the bond valence sum (BVS) calculation gives a value of 2.98 and 2.93 for Eu1 and Eu2 respectively [12]. If the eighth bond length is considered, the BVS value is equal to 3.19 for Eu1 and Eu2. The values of 2.98 and 2.93 being closer to 3, a coordination number (CN) of 7 could be considered. However in the description of isotypic compounds, a coordination number equal to 8 was considered. To determine the best coordination number of each lanthanide and yttrium ions, different calculations of bond valence sum have been realized. The results will be presented later in the discussion. At this step, considering seven oxygen atoms in the coordination sphere, the polyhedron may be described as a distorted monocapped trigonal prism. The dihedral angle between the two trigonal faces is equal to 10.6° and 18.1° for Eu1 and Eu2, respectively. With eight oxygen atoms, the polyhedron is described as a square antiprism. The mean deviations of the square planes are equal to 0.033 Å and 0.146 Å for Eu1 (faces defined by (O1, $O1^{IV}$, $O12^{II}$ and O2) and (O11, $O14^{I}$, O21 and $O24^{III}$) respectively) and equal to 0.073 Å and 0.165 Å for Eu2 (faces defined by (O1, O2, $O2^{VII}$ and $O22^{V}$) and ($O11^{VII}$, $O13^{VI}$, $O21^{VII}$ and $O23^{II}$) respectively). The dihedral angle between these two faces is equal to 5.44° and 4.97° for Eu1 and Eu2, respectively. The eight CN is considered since the distortion of the square antiprism polyhedron is lower than the monocapped trigonal prism one.

The $[CrO_4]^{2-}$ chromate groups possess the usual tetrahedral geometry. For Cr1 and Cr2 respectively, the Cr-O mean bond lengths are 1.642(8) Å and 1.648(7) Å (Table 1) and the O-Cr-

O angles are ranged from 107.4(4)° to 113.0(4)° and from 106.9(4)° to 112.1(4)°. Both chromate groups coordinate three europium cations in a monodentate way and the fourth oxygen atom bridges two europium cations.

Each oxygen atom of the hydroxyl groups coordinates three europium cations. The Eu-O1(H)-Eu angles are equal to 99.7(4)°, 104.3(4)° and 135.6(4)°, and the Eu-O2(H)-Eu angles are 102.5(4)°, 105.7(4)° and 110.0(4)°. One Eu-O1(H)-Eu angle deviates from the tetrahedral geometry, as for *Ln*(OH)(CrO_4) (*Ln* = Nd and Yb) [10-11], due to a rigid double chromate bridge between these two Eu atoms.

The [(Eu1)O_8] and [(Eu2)O_8] polyhedra form double chains along the *a* direction by edge and corner-sharing (Fig. 1), alternating [(Eu1)O_8] and [(Eu2)O_8] polyhedra in each chain. The [(Eu1)O_8] polyhedron shares two edges with another [(Eu1)O_8] and one [(Eu2)O_8] polyhedra and two corners with two [(Eu2)O_8] polyhedra. Reversely each [(Eu2)O_8] polyhedron shares two edges with one [(Eu1)O_8] and another [(Eu2)O_8] polyhedra and two corners with two [(Eu1)O_8] polyhedra. These double chains are related together by corner-sharing with the $[CrO_4]^{2-}$ tetrahedra in the two other directions leading to the formation of a three-dimensional network. The four chromate oxygen atoms are involved in these connections. Each $[(Cr1)O_4]^{2-}$ tetrahedra are connected to three [(Eu1)O_8] and two [(Eu2)O_8] polyhedra and each $[(Cr2)O_4]^{2-}$ tetrahedra are related to three [(Eu2)O_8] and two [(Eu1)O_8] polyhedra. Each europium atom is bridged to sixteen other europium atoms either by chromate groups or by hydroxyl oxygen atoms with distances ranging from 3.732(8) Å to 7.522(8) Å. Europium and chromium polyhedra form pentagonal and tetragonal channels parallel to the *a* direction; hydrogen atoms lie in the first type of channel (Fig. 1). Hydroxyl functions establish a hydrogen bond network with chromate oxygen atoms, evidenced by the O···O distances (2.704(7) to 2.990(7) Å). O1(H) and O2(H) are

surrounded by four and five oxygen atoms respectively with distances shorter than 3.0 Å. The number of oxygen atoms around the hydroxyl groups in *Ln*(OH)(CrO_4) (*Ln* = Nd, Gd, Tb, Er and Yb) [8-11] increases with the atomic number of the lanthanide, ranging up to eight oxygen atoms in the Yb(OH)(CrO_4) structure [11].

To confirm the coordination number of lanthanide and yttrium ions equal to eight, BVS calculations have been realized with three different methods based on Brese's [12], Adams's [13-14] and the recently reported Zocchi's works [15]. The Brese's method is the most often used. In Adams's approach, a correlation between *B* and the absolute softnesses of the interacting atoms is established and provides somewhat lower BV values than the conventional data. In his article, Zocchi propose a dependence of the R_1 and *B* parameters on the coordination numbers for *Ln*-O bonds. Results are presented in Table 2 and Figure 2. With the Brese's method, it appears that the best value obtained for the valence of lanthanide and yttrium ions (expected value = 3.00) corresponds to a same coordination number equal to 7. The Adams's method leads to a CN equal to 8 for all lanthanide and yttrium ions. Zocchi's parameters lead to intermediate results: the BVS values are closer to 3 with a CN equal to 7 and 8 for biggest Nd, Eu and Gd ions and for smallest Tb, Er and Yb ions, respectively. Due to the lanthanide contraction, the coordination number can't increase while the ionic radius decreases. Effectively, it is shown with the linear decreasing of the unit cell volume with the ionic radius of lanthanide (Fig.3). Yttrium ion was also presented on this figure in order to compare with the family of lanthanides. In this case, it is reasonable to consider a same CN for all lanthanide and yttrium ions. Finally, taking into account the best geometry of the coordination polyhedron formed by the ligands (square antiprism), the best CN to be considered is 8.

Unlike to the chromate compounds, the previously studied lanthanide iodates α-*Ln*$(IO_3)_3$ and β-*Ln*$(IO_3)_3$ (*Ln* = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) [16] demonstrate a change of CN between europium and gadolinium ions. For largest cations, the CN is equal to 8 and for the smallest, it is equal to 7. In the *Ln*(OH)(CrO_4) compounds, *a* and *c* parameters increase faster than *b* parameter with the ionic radius (Δa(Yb-Nd) = 0.311 Å; Δb(Yb-Nd) = 0.128 Å and Δc(Yb-Nd) = 0.359 Å) whereas the β angle slightly increases from 93.73° for Nd to 94.27° for Yb [8-11].

Conclusion

The Eu(OH)(CrO_4) and Y(OH)(CrO_4) compounds were obtained under hydrothermal conditions. The crystal structures show they are isostructural with other *Ln*(OH)(CrO_4) compounds (*Ln* = Nd, Gd, Tb, Er and Yb). We examine the structural evolution, as a function of the Ln^{3+} ionic radius, in the series *Ln*(OH)(CrO_4) compounds. Calculations of bond valence sum allow us to confirm a coordination number of each lanthanide and yttrium ions equal to 8. The unit cell volume decrease linearly with the ionic radius of lanthanide.

Due to their centrosymmetric structures, the Y(OH)(CrO_4) and *Ln*(OH)(CrO_4) compounds are unusable as quadratic NLO materials. However as they are isostructural, $Y_{1-x}Ln_x$(OH)(CrO_4) solid solutions could be prepare. So, the interest of these bimetallic compounds is the preparation of new laser crystals, the yttrium chromate can be used as host matrix as realized with $Y(IO_3)_3$ [17]. All lanthanide combinations could be inserted in order to vary the luminescence properties of as-prepared materials.

Experimental Section

Synthesis of $Eu(OH)(CrO_4)$

$Eu(OH)(CrO_4)$ has been obtained in two steps. The first one leads to the formation of $KEu(CrO_4)_2$. The reaction takes place in the solid state. This compound, which has already been characterized by Bueno et al. [18], was prepared by mixing CrO_3, Eu_2O_3 and KNO_3 (2:1/2:1) powders in an agate mortar. Then the mixture was heated in a furnace under air at 500°C during 18 hours. A green powder was obtained and 53 mg was put in 10 mL of water into a Teflon-lined steel autoclave. After sealing, the autoclave was heated to 130°C in oven and held 18 hours at this temperature. Then the autoclave was gradually cooled at 10°C/h down to 50°C. A green solution was obtained containing a green powder ($KEu(CrO_4)_2$ remaining powder), orange square platelets ($Eu(OH)(CrO_4)$) and yellow rod crystals (K_2CrO_4, JCPDS file no. 01-089-8260). This solution was filtered and solid part was washed with deionised water and dried in furnace. Platelets were separated under binocular.

Synthesis of $Y(OH)(CrO_4)$

$Y(OH)(CrO_4)$ has been obtained in one step. A mixing of Y_2O_3 (112 mg) and $Na_2Cr_2O_7$ (1.310 g) (Y:Na, 1:10 molar ratio) powders in 10 mL of water was put into a Teflon-lined steel autoclave. After sealing, the autoclave was heated to 200°C in oven and held 5 days at this temperature. After cooling, a yellow solution was obtained containing an amorphous yellow powder, orange square platelets ($Y(OH)(CrO_4)$) and yellow rod crystals (Na_2CrO_4, JCPDS file no. 01-072-0593). This solution was filtered and solid part was washed with deionised water and dried in furnace. Platelets were separated under binocular.

Crystal structure determination

Crystal data and details of the data collections and refinements are summarized in Table 3. Crystals of $Eu(OH)(CrO_4)$ and $Y(OH)(CrO_4)$ were mounted, at 293 K, on a NONIUS k-CCD diffractometer using monochromatic silver radiation (λ = 0.56087 Å) for the first compound and monochromatic molybdenum radiation (λ = 0.71073 Å) for the second one. The reflections were corrected for Lorentz and polarization effects. An absorption correction was applied using the Gaussian integration method [19]. Both structures were solved by direct methods with the SIR92 program [20] and refined by full-matrix least-squares, based on F^2, using the SHELXL software [21] through the WinGX program suite [22]. Refinements were performed with anisotropic thermal parameters for all non-hydrogen atoms.

[1)] Structure representation is made with Diamond software, version 3.1f [23].

[2)] Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-421744 and CSD-421743, the names of the authors and citation of the publication.

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Table 1 Selected bond lengths (Å) (with e.s.d) in *M*(OH)(CrO_4) (*M* = Y, Eu) (e.s.ds. in parentheses)

Atom 1	Atom 2	Y	Eu
Ln1	O14^{I}	2.251(6)	2.321(8)
	O12^{II}	2.325(6)	2.366(8)
	O2(H)	2.315(5)	*2.378(6)*
	O11	2.338(5)	2.389(6)
	O24^{III}	2.363(6)	2.429(7)
	O1(H)	2.376(6)	2.435(7)
	O1(H)^{IV}	2.405(5)	2.446(6)
	O21	2.640(6)	2.640(7)
Ln2	O23^{II}	2.306(6)	2.349(7)
	O22^{V}	2.305(6)	2.358(7)
	O2(H)	2.299(6)	2.360(7)
	O13^{VI}	2.346(6)	2.385(8)
	O2(H)^{VII}	2.367(5)	2.419(6)
	O21^{VII}	2.386(5)	2.456(7)
	O1(H)	2.433(5)	2.481(6)
	O11^{VII}	2.571(5)	2.572(7)
Cr1	O13	1.631(6)	1.618(7)
	O12	1.632(6)	1.627(8)
	O14	1.652(6)	1.636(8)
	O11	1.678(5)	1.685(7)
Cr2	O22	1.629(6)	1.630/7)
	O24	1.633(5)	1.631(7)
	O23	1.651(6)	1.652(7)
	O21	1.684(6)	1.679(7)

Equivalent positions are I: (x-1/2, -y-1/2, z-1/2); II (-x+1/2, y+1/2, -z+1/2); III (x-1/2, -y+1/2, z+1/2); IV (-x, -y+1, -z+1);V (x, y , z+1); VI (-x+1/2, y+1/2, -z+3/2); VII (-x+1, -y+1, -z+1).

Table 2 *Ln*-O bond lengths and BVS of *Ln* calculated for a CN equal to 7 and 8, with three methods, in $Ln(OH)(CrO_4)$ (*Ln* = Nd, Eu, Gd, Tb, Er and Yb) and in $Y(OH)(CrO_4)$

Element / atomic number (Z)	Volume of the unit cell (Å^3)	Atoms	Range of bond lengths for the seven shorter bonds (Å)	Bond length for the eighth bond (Å)	BVS[e]/ BVS[f]/BVS[g] for CN=7	BVS[e] / BVS[f]/BVS[g] for CN=8
Nd[a] / 60	816.5(4)	Nd1	2.353 – 2.500	2.670	2.95 / 2.67/ 2.91	3.18 / 2.89/ 3.17
		Nd2	2.398 – 2.505	2.610	2.93 /2.65/ 2.88	3.19 / 2.91/ 3.18
Eu / 63	790.3(3)	Eu1	2.321 – 2.446	2.640	2.98 / 2.86/ 2.97	3.19 / 3.09/ 3.14
		Eu2	2.349 – 2.481	2.572	2.93 / 2.82/ 2.92	3.19 / 3.09/ 3.13
Gd[b] / 64	783.2(1)	Gd1	2.304 – 2.442	2.643	3.01 / 2.79/ 2.97	3.22 / 3.00/ 3.11
		Gd2	2.340 – 2.457	2.571	2.96 / 2.75/ 2.91	3.21 / 3.00/ 3.10
Tb[b] / 65	774.7(2)	Tb1	2.290 – 2.429	2.628	2.99 / 2.73/ 2.94	3.20 / 2.94/ 3.03
		Tb2	2.326 – 2.455	2.558	2.95 / 2.70/ 2.89	3.20 / 2.94/ 3.08
Y / 39	765.2(2)	Y1	2.251 – 2.405	2.640	3.01 / 2.83/ -	3.19 / 3.04/ -
		Y2	2.299 – 2.433	2.571	2.91 / 2.77/ -	3.15 / 3.02/ -
Er[c] / 68	755.4(3)	Er1	2.251 – 2.378	2.636	3.00 / 2.87/ 2.90	3.18 / 3.06 / 3.15
		Er2	2.289 – 2.432	2.533	2.90 / 2.78/ 2.79	3.14 / 3.03/ 3.09
Yb[d] / 70	744.2(1)	Yb1	2.224 – 2.373	2.620	2.98 / 2.92/ 2.85	3.16 / 3.12/ 3.02
		Yb2	2.268 – 2.409	2.544	2.88 / 2.83/ 2.74	3.10 / 3.07/ 2.95

[a] Ref. [10], [b] Ref. [9], [c] Ref. [8], [d] Ref. [11], [e] Ref.[12], [f] Ref. [13-14], [g] Ref. [15]

Table 3 Crystal data and structure refinement details for $Eu(OH)(CrO_4)$ and $Y(OH)(CrO_4)$

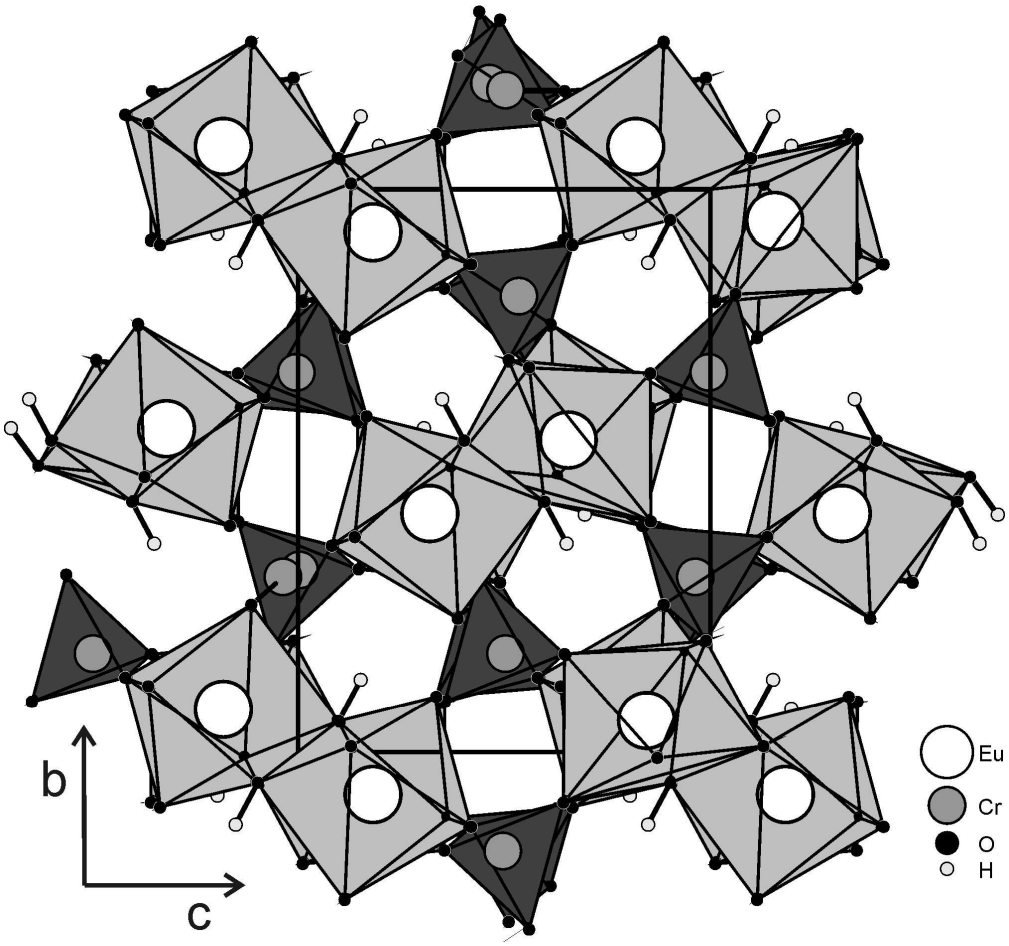
Formula	$Eu(OH)(CrO_4)$	$Y(OH)(CrO_4)$
M /g.mol^{-1}	569.94	443.84
Crystal system	monoclinic	monoclinic
Space group	$P2_1$/n (no. 14)	$P2_1$/n (no. 14)
a /Å	8.278(1)	8.151(1)
b /Å	11.400(2)	11.362(2)
c /Å	8.393(1)	8.285(1)
β / °	93.76(2)	94.23(1)
V /Å^3	790.3(2)	765.2(2)
Z	8	8
ρ_{calcd} (g.cm^{-3})	4.79	3.853
μ /mm^{-1}	9.729	17.818
θ range for data	3.15 – 21.4	3.05 – 30
$N_{hkl,collected}$	10022	8486
$N_{hkl,unique}$ (I>2σ(I))	1568	1427
R_{int}	0.0747	0.1038
Refined parameters	127	127
R_1 ($I > 2\sigma(I)$)	0.0352	0.0556
wR_2 (all data)	0.0838	0.1409
Goodness of fit on F^2	1.26	1.037
$\Delta\rho_{max}/\Delta\rho_{min}$ (e.Å^{-3})	1.855/-1.253	1.634/-1.909

Figure Captions:

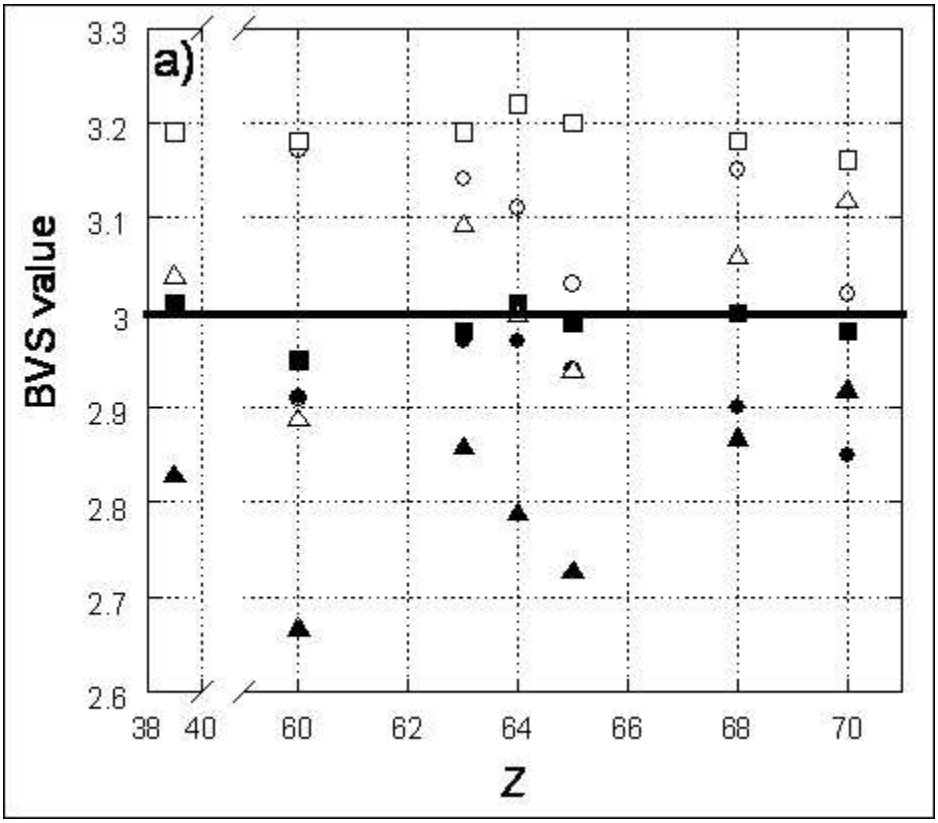
Fig. 1 Crystal structure of $Eu(OH)(CrO_4)$, view in *a* direction.

Fig. 2 Evolution of the BVS values for metal ions in $Y(OH)(CrO_4)$ and $Ln(OH)(CrO_4)$ (*Ln* = Nd, Eu, Gd, Tb, Er and Yb) calculated with three methods [12, 15] *versus* atomic number of elements. Brese's method with CN=8 (□), CN=7 (■), Adams's method with CN=8 (Δ), CN=7 (▲), Zocchi's method with CN=8 (○), CN=7(●). The a) and b) graphs correspond to the metal atom number 1 and 2 respectively.

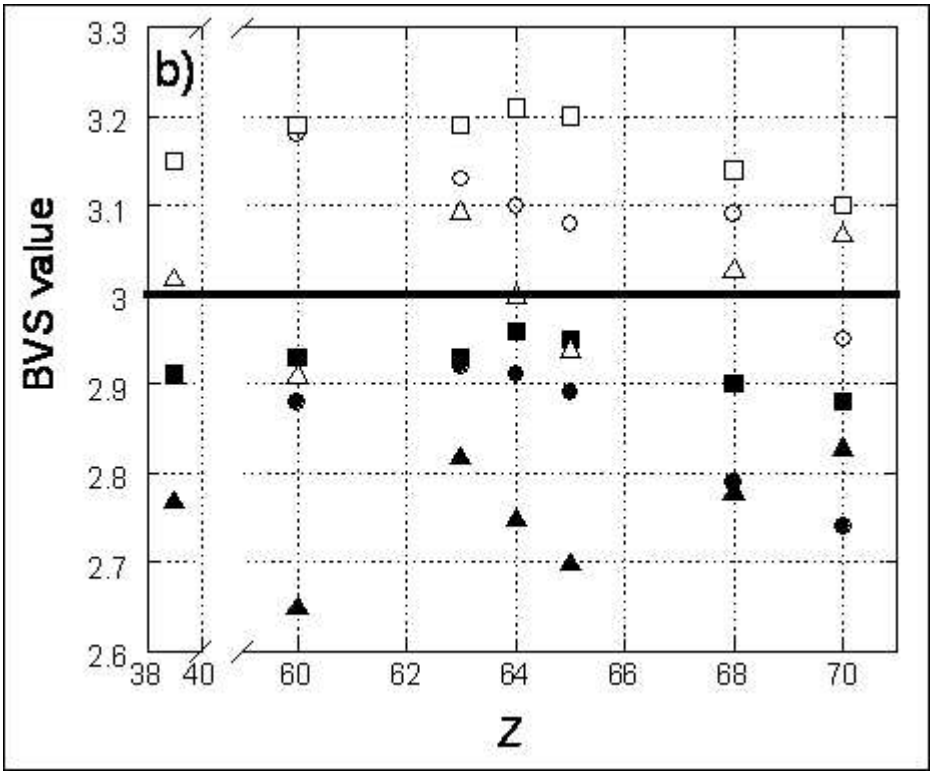
Fig. 3 Evolution of the unit cell volume for $Ln(OH)(CrO_4)$ (*Ln* = Nd, Eu, Gd, Tb, Er and Yb) and $Y(OH)(CrO_4)$ *versus* ionic radius (CN = 8), refined from single crystal X-ray diffraction.



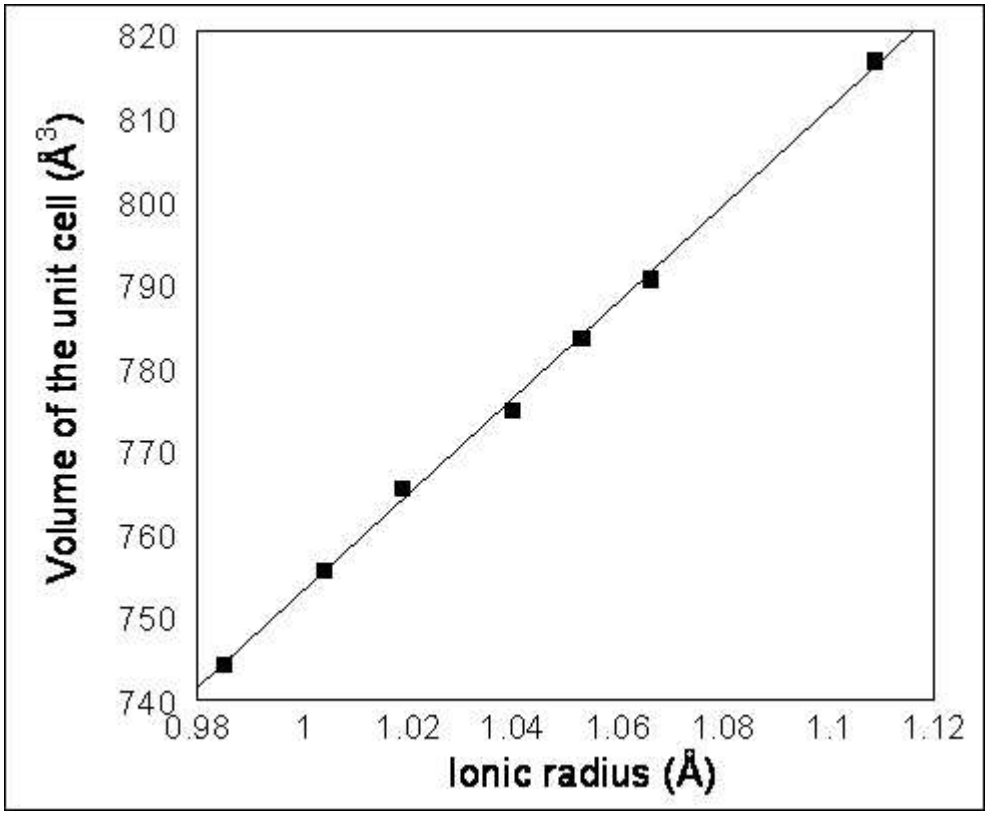
Crystal structure of Eu(OH)(CrO4), view in a direction
85x79mm (600 x 600 DPI)



78x68mm (150 x 150 DPI)



Evolution of the BVS values for metal ions in Y(OH)(CrO4) and Ln(OH)(CrO4) (Ln = Nd, Eu, Gd, Tb, Er and Yb) calculated with three methods [12, 15] versus atomic number of elements. Brese's method with CN=8 (□), CN=7 (■), Adams's method with CN=8 (Δ), CN=7 (▲), Zocchi's method with CN=8 (○), CN=7(●). The a) and b) graphs correspond to the metal atom number 1 and 2 respectively.
78x64mm (150 x 150 DPI)



Evolution of the unit cell volume for Ln(OH)(CrO4) (Ln = Nd, Eu, Gd, Tb, Er and Yb) and Y(OH)(CrO4) versus ionic radius (CN = 8), refined from single crystal X-ray diffraction.
82x68mm (150 x 150 DPI)