Structural Chemistry and Magnetism of Tb^{3+}-β''-Alumina ($Tb_{0.46}Al_{10.62}Mg_{0.38}O_{17}$)

Frank Soetebier[a] **and Werner Urland***[a]

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The structure of completely exchanged Tb^{3+}-β''-Al_2O_3 ($Tb_{0.46}Al_{10.62}Mg_{0.38}O_{17}$) crystals has been investigated by single crystal X-ray diffraction methods at room temperature [trigonal, $R\bar{3}m$, $Z = 3$, $a = 560.91(8)$ pm, $c = 3330.3(8)$ pm]. The terbium ions are found to occupy BR (49.2%) and mO positions (50.8%) in nearly the same amount. The structural results are discussed in relation to magnetic measurements on crushed single crystals, where ligand field calculations applying the angular overlap model have been taken into account.

Introduction

The fast ion conductor Na^+-β''-Al_2O_3, so-called β''-alumina, is generally described by the formula given by Bettman and Peters as $Na_{1+x}Mg_xAl_{11-x}O_{17}$ (x = 0.24−0.7).[1] It crystallizes in the trigonal space group $R\bar{3}m$ and consists of close-packed spinel blocks separated by conduction planes containing the mobile Na^+ cations. Covalent Al−O−Al bonds and Coulomb attraction forces of the in-plane cations to the spinel bock anions connect the blocks. Due to the high mobility of the Na^+ ions they can be replaced by other mono-, di- and trivalent cations, especially by lanthanide ions (Ln^{3+}).[2,3] There are two possible crystallographic positions for the cations within the conduction plane: the sevenfold coordinated (smaller) Beevers−Ross (BR) site (C_{3v} symmetry, 6c Wyckoff notation in $R\bar{3}m$) and the eightfold coordinated (larger) mid-Oxygen (mO) site (C_{2h} symmetry, 9d Wyckoff notation in $R\bar{3}m$). The content of Na^+ cations affects the height of the conduction slabs and therefore the lattice constant c.[4]

Previous investigations on Ln^{3+}-exchanged compounds like La^{3+}-β''-Al_2O_3,[5] Pr^{3+}-β''-Al_2O_3,[6] Nd^{3+}-β''-Al_2O_3, Eu^{3+}-β''-Al_2O_3 and Gd^{3+}-β''-Al_2O_3 [7] show a main occupation of the higher coordinated mO site. In this paper the structure and the magnetic behaviour of completely exchanged Tb^{3+}-β''-Al_2O_3 single crystals are presented. The determination of the ionic distribution within the conduction plane is important to understand the mobility of trivalent cations.[8,9] The observed occupancy is correlated with susceptibility measurements on crushed Tb^{3+}-β''-Al_2O_3 crystals where ligand-field calculations applying the angular overlap model (AOM) for f-electrons[10−12] have been taken into account.

Results and Discussion

The structure of the spinel blocks (Mg/Al distributions, vacancies, etc.) is similar to other β''-aluminas studied before and will therefore not be discussed in further detail. The ion distribution within the conduction planes (*ab*-planes) is of main interest. The structural refinements lead to a distribution of 49.2% Tb^{3+} cations on the smaller BR site and 50.8% on the larger mO site. Due to the nearly equal atomic form factors, Mg^{2+} and Al^{3+} ions within the spinel blocks were not distinguishable. Because of charge neutrality the Mg^{2+} content could be estimated from the refined cationic/anionic occupancy ratio. This results in the formula $Tb_{0.46}Al_{10.62}Mg_{0.38}O_{17}$. The site multiplicities, fractional atomic coordinates, site occupation factors and equivalent displacement parameters are given in Table 1, some interatomic distances are shown in Table 2.

Table 1. Site multiplicities, fractional atomic coordinates, site occupation factors (s.o.f.) and equivalent displacement parameters [pm^2] for $Tb_{0.46}Al_{10.62}Mg_{0.38}O_{17}$

Atom	site	x/a	y/b	z/c	s.o.f	U_{eq}
Tb1	6c	0	0	0.1781(3)	0.091(4)	230(30)
Tb2	9d	5/6	1/6	1/6	0.094(4)	580(40)
Al1	3a	0	0	0	1	50(12)
Al2	6c	0	0	0.3506(1)	1	68(10)
Al3	18h	0.3350(4)	0.5 x/a	0.0721(2)	1	86(8)
Al4	6c	0	0	0.4516(1)	1	91(10)
O1	18h	0.1539(5)	2 x/a	0.0350(2)	1	116(13)
O2	6c	0	0	0.2950(2)	1	78(19)
O3	6c	0	0	0.0981(2)	1	100(20)
O4	18h	0.1632(5)	2 x/a	0.2346(1)	1	87(13)
O5	3b	1/3	2/3	1/6	1	2400(400)

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[a] Institut für Anorganische Chemie der Universität Hannover,
Callinstrasse 9, 30167 Hannover, Germany
Fax: (internat.) + 49-(0)511/762-19032
E-mail: urland@acc.uni-hannover.de

Table 2. Selected interatomic distances [pm] in $Tb_{0.46}Al_{10.62}Mg_{0.38}O_{17}$

Tb1−O3 (1x)	266.5(13)
Tb1−O4 (3x)	246.0(9)
Tb1−O5 (3x)	326.0(1)
Tb2−O3 (2x)	279.9(7)
Tb2−O4 (4x)	277.2(4)
Tb2−O5 (2x)	280.5(1)
Al1−O1 (6x)	189.6(4)
Al2−O1 (3x)	184.1(6)
Al2−O2 (1x)	185.2(9)
Al3−O1 (2x)	199.4(4)
Al3−O2 (1x)	196.4(5)
Al3−O3 (1x)	184.3(4)
Al3−O4 (2x)	182.9(3)
Al4−O4 (3x)	177.6(5)
Al4−O5 (1x)	161.0(4)

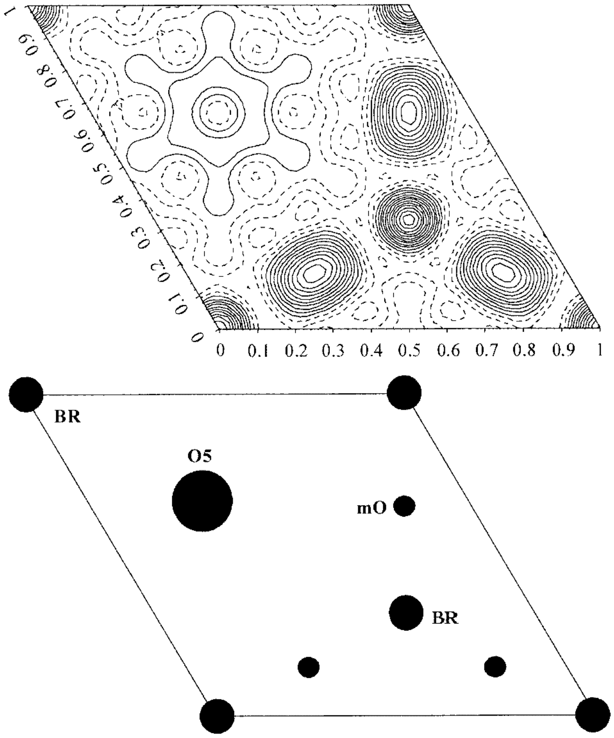

Figure 1. Electron density map (ρ_{obs}) of the conduction plane (z = 1/6); the contour intervals are 1 $e\cdot\AA^{-3}$; a schematic representation of the occupied sites is given beneath

As can be seen from Figure 1 the electron density is extended for all positions in the conduction plane, indicating large local disordering induced by Coulomb interactions between the ions. The Tb^{3+} ions in the mO sites are shifted towards neighbouring empty BR positions. The sites of the column oxygens O5 are influenced by the local cation environment, leading to large displacement parameters.

We observed that the size and the ionic distribution (BR/mO ratio) of the lanthanide ions are correlated with each other. The larger cations such as Nd^{3+} ions prefer the eightfold coordinated mO site (93%)[7] and the smaller ones (for example Ho^{3+} ions) the sevenfold coordinated BR site (84%).[13] Thus the BR/mO ratio of 49.2:50.8 found here for the terbium ion distribution is in line with previous findings.

From these results the ionic conductivity of La^{3+}-β′′-Al_2O_3,[5] Pr^{3+}-β′′-Al_2O_3 [14] and Ho^{3+}-β′′-Al_2O_3,[15,16] which differs in the temperature at which lanthanide ion mobility begins (574 K for La^{3+}, 564 K for Pr^{3+} and 496 K for Ho^{3+}), can be explained: the decrease of this temperature is due to an easier occupation of the BR site with smaller cations.

Magnetic susceptibility measurements on crushed single crystals were performed with a SQUID magnetometer in the 2.0−300.0 K temperature range at field strengths of 2 and 5 kOe. The magnetic susceptibilities are practically independent of the magnetic field (see Figure 2). In order to interpret the measured susceptibilities we carried out ligand-field calculations applying the angular overlap model within the basis set ^7F for Tb^{3+} and using the spin-orbit coupling constant of 1705 cm^{-1}.[17] The angular overlap parameters e_σ and e_π (Table 3) representing σ- and π-bonding between terbium ions and coordinated oxygen atoms were obtained by fitting procedures using the spiral algorithm.[18] The theoretical susceptibilities for both sites (BR and mO site) were calculated and fitted to the measured data. These were added up according to the occupancy ratio obtained from the structural investigation. The good agreement between the observed and calculated (fitted) inverse susceptibilities (R value:[19] 0.62%) of Tb^{3+}-β′′-Al_2O_3 is shown in Figure 2.

Table 3. Angular overlap parameters e_σ and e_π [cm^{-1}] for $Tb_{0.46}Al_{10.62}Mg_{0.38}O_{17}$

	e_σ	e_π
Tb1(BR)−O_S [a]	630	270
Tb1(BR)−O_C	536	142
Tb2(mO)−O_S	252	73
Tb2(mO)−O_C	341	79

[a] O_S: spinel block oxygen atoms (O3, O4), O_C: conduction plane oxygen atoms (O5).

The calculated e_σ/e_π ratios range between 2.3 and 4.3, in line with values for other lanthanide compounds (2.66 for $LaCl_3:Tb^{3+}$,[20] 2.89 for $CaWO_4:Tb^{3+}$,[21] 3.4 for $TbAl_3Cl_{12}$ [17]). Assuming a d^{-7} dependency of e_σ [21] (where d represents the distance between Tb^{3+} and coordinated oxygen atom) and taking $d[Tb^{3+}(BR)-O_S]$ = 251 pm and $d[Tb^{3+}(mO)-O_S]$ = 278 pm (averaged from Table 2) we obtain from Table 3 values for $d[Tb^{3+}(BR)-O_C]$ = 257 pm and $d[Tb^{3+}(mO)-O_C]$ = 266 pm. These calculated distances are smaller than the crystallographic ones (cf. Table 2). This is because the partial occupation of the BR and mO sites leads to a local coordination of the Tb^{3+} ions because of Coulomb attraction and this differs from the

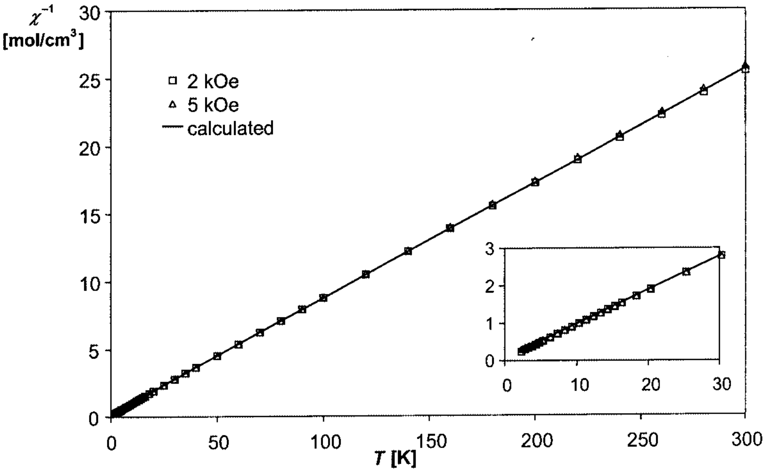

Figure 2. Observed inverse magnetic susceptibilities at different field strengths and calculated values for $Tb_{0.46}Al_{10.62}Mg_{0.38}O_{17}$ (−)

averaged coordination observed by X-ray investigation. This expresses itself in the low displacement parameters of O_S (see O3, O4 in Table 1) and the large ones of O_C (see O5 in Table 1).

Experimental Section

Na^+-β′′-Al_2O_3 (1): Na^+-β′′-alumina crystals were grown by flux evaporation from a mixture of 32.4 mol % Na_2O (from Na_2CO_3, Chempur, 99.99%), 8.0 mol % MgO (Chempur, 99.99%) and 59.6 mol % Al_2O_3 (Chempur, 99.99+%). The Na_2O-rich flux was heated for 19 days in a platinum foil coated crucible of corundum at 1680 °C according to an empirical temperature program.[22]

Tb^{3+}-β′′-Al_2O_3 (2): For the ion-exchange reaction a platinum net containing clear and colourless crystals of **1** was immersed under an argon atmosphere in an anhydrous $TbCl_3$ melt (Aldrich, 99.99%). To ensure a nearly complete exchange the crystals were exposed to the melt for 72 hours at 650 °C. No further heat treatments were applied after quenching the crystals to room temperature.

Magnetic Measurements: Measurements of the magnetic susceptibility were performed with a SQUID magnetometer (MPMS5, Quantum Design) in the 2.0 to 300 K temperature range at field strengths of 2 and 5 kOe. A polycrystalline sample of crushed single crystals was placed in a gelatine capsule and fixed with conventional cotton wool. The raw magnetic data were corrected for diamagnetism by measuring susceptibilities of Na^+-β′′-Al_2O_3.

X-ray Crystallographic Study: Crystallographic data were collected with a Stoe-IPDS diffractometer at room temperature. An optical clear single crystal was chosen for X-ray measurements. For details of the measurement see Table 4. The initial parameters used in the least-squares refinement of the spinel blocks and the bridging oxygen ions (O5) were taken from published parameters of Na^+-β′′-Al_2O_3.[1] BR and mO positions were occupied with Tb^{3+} ions (Tb1 and Tb2, respectively). The final refinement results in a distribution of 49.2% Tb^{3+} cations on the smaller BR site and 50.8% on the larger mO site. Due to the nearly equal atomic form factors, Mg^{2+} and Al^{3+} ions within the spinel blocks were not distinguishable. Because of charge neutrality the Mg^{2+} content could be estimated from the refined cationic/anionic occupancy ratio. The atomic sites, coordinates, site occupation factors, equivalent displacement parameters and selected interatomic distances are shown in Table 1 and 2.

Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-412282.

Table 4. Crystallographic data for $Tb_{0.46}Al_{10.62}Mg_{0.38}O_{17}$

Compound	$Tb_{0.46}Al_{10.62}Mg_{0.38}O_{17}$
Crystal system	trigonal
Space group	$R\bar{3}m$
Lattice constants [pm]	$a = 560.91(8)$ $c = 3330.3(8)$
V [pm³]	$907.4(3)\cdot 10^6$
Z	3
ρ (X-ray) [g/cm³]	3.527
Absorption coefficient [μ/mm⁻¹]	3.681
$F(000)$	927
Crystal dimensions [mm³]	0.241·0.518·0.047
Diffractometer	Stoe-IPDS
Temperature [K]	293(2)
Wavelength	Mo-K_α ($\lambda = 71.073$ pm)
θ range [°]	$3.3 \leq 2\theta \leq 52.1$
Index range (h, k, l)	±6, ±6, ±40
R_{int}	0.1116
No. of collected reflections	4237
No. of independent reflections	261
Observed reflections with $F>2\sigma$	248
Absorption correction	numerical
Structure refinement	Full-matrix, least-squares
Programs used	SHELXS-97[23] and SHELXL-97[24]
No. of refined parameters	44
Goodness-of-fit	1.236
R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0646$; $wR_2 = 0.1688$
R_1, wR_2 (all data)	$R_1 = 0.0666$; $wR_2 = 0.1703$
Min., max Δ ρ [e·pm⁻³·10⁻⁶]	−1.115/1.748

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