Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Synchrotron study of pyrochlore-related $NaCdZn_2F_7$

K. Friese,[a]* A. Grzechnik,[a] W. Morgenroth,[b] G. Buth,[c] S. Doyle[c] and J.-Y. Gesland[d]

[a]Departamento Física Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644, E-48080 Bilbao, Spain, [b]Hasylab am DESY, Notkestraße 85, D-22607 Hamburg, Germany, [c]Forschungszentrum Karlsruhe GmbH, Institute for Synchrotron Radiation, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany, and [d]Université du Maine-Cristallogenese, UMR 6087, F-72025 Le Mans Cedex 9, France

Correspondence e-mail: wmbfrxxk@lg.ehu.es

Received 21 June 2005
Accepted 18 July 2005
Online 23 July 2005

The crystal structure of pyrochlore-related $NaCdZn_2F_7$ (sodium cadmium dizinc heptafluoride) has been determined *via* synchrotron diffraction. Zn is octahedrally coordinated by fluorine. Na and Cd are both coordinated by eight anions. Despite the different chemical characteristics and valences, no indication of ordering of Na and Cd was observed.

Key indicators

Single-crystal synchrotron study
T = 293 K
Mean σ(Zn–F) = 0.001 Å
Disorder in main residue
R factor = 0.032
wR factor = 0.039
Data-to-parameter ratio = 36.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Numerous compounds with structures related to that of the mineral pyrochlore are known. The ideal pyrochlore structure has the general formula $A_2B_2X_7$, where A = Na, Ca, Sr, Mg, Pb *etc*., B = Nb, Ta, Ti, Fe, Zr *etc*., and X = O, F and OH^-. The A site is coordinated by eight anions, while the B site is octahedrally coordinated by six anions.

Within the fluorine representatives of this family, substitutions of different cations are possible both on the A and on the B site. If, for instance, a large cation, such as Cs^+ or Rb^+, is incorporated into one of the A sites (the other remaining empty), the modified pyrochlore structures with general formula $AB^{2+}B^{3+}F_6$ are obtained, where it is generally transition metal ions that are incorporated into the B site. Several compounds of this general composition are known [an overview is given in Table 1 of Friese *et al.* (2005)]. As long as the two types of cations on the B sites are perfectly disordered, the high cubic symmetry of the ideal pyrochlore structure is not violated. Ordering of the cations, however, leads to a lowering to orthorhombic symmetry and, in the case of $KCuCrF_6$ (Kissel & Hoppe, 1988), even to monoclinic symmetry. The compound $CsMgInF_6$, which was recently investigated by us (Friese *et al.*, 2005), is a remarkable representative of this family, as no ordering of the cations at the B site could be observed, although its symmetry is lowered to orthorhombic.

The incorporation of different cations on the A site is also possible. However, only two members with general composition $(A_{0.5}{}^{+}A'_{0.5}{}^{2+})_2B^{2+}{}_2F_7$ are known, *viz*. $NaSrMg_2F_7$ (Kubel & Dundjerski, 2001) and $NaCaMg_2F_7$ (Oliveira *et al.*, 2004). Na/Sr and Na/Ca are randomly distributed over the A sites and, despite the considerable differences between the monovalent and divalent cations, no indications of ordering have been observed.

The subject of this investigation is a compound with the nominal composition $NaCdZn_2F_7$. Although the disordered incorporation of Na and Cd on one singular site has already been observed in other compounds, such as Na_2CdYbF_7 (Koch & Hebecker, 1992), $NaCaCdYF_8$ (Hund & Lieck, 1952), $Cd_4Na(VO_4)_3$ (Ben Amara *et al.*, 1979; Abrahams *et al.*, 1983), $Cd_{3.23}Na_{1.41}V_{0.36}(VO_4)_3$ (El Ammari *et al.*, 1999) and $Na_{0.55}Cd_{2.45}P_2O_{7.45}(OH)_{0.55}$ (Ivanov *et al.*, 1976), we thought it worthwhile to carry out very precise and detailed investiga-

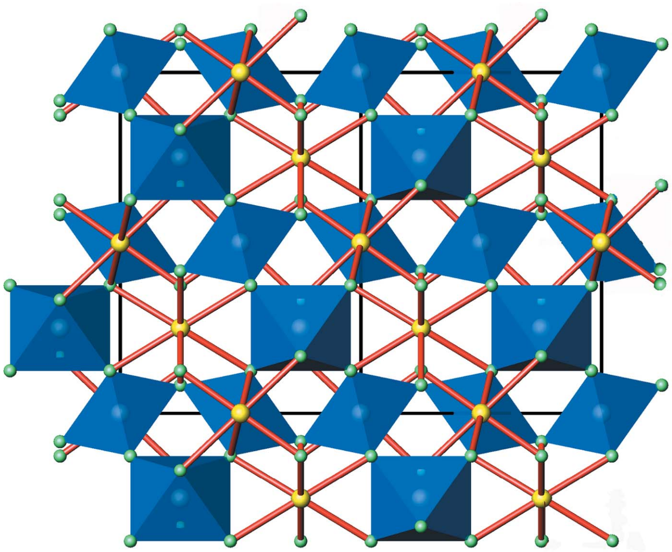

Figure 1
Projection of the structure of $NaCdZn_2F_7$ along the $[1\bar{1}0]$ direction. Octahedra around Zn (blue) are shown. Bonds from Na (yellow) to flourine (turqoize) are indicated.

tions to confirm the absence/presence of additional ordering of these two cations. Therefore, we decided to perform not only conventional laboratory experiments but also synchrotron radiation studies. To detect possible diffuse scattering originating from the ordering of the two cations, we used an image-plate detector at the synchrotron at Anka, Karlsruhe, Germany. For accurate structure determination, we measured intensities with a scintillation counter up to high diffraction angles at Hasylab, Hamburg, Germany.

The structural refinement on the basis of these data confirms the close relation of the structure to the pyrochlore structure type (see Fig. 1). Zn is incorporated into the *B* sites and is coordinated by six F2 ions in the form of a slightly distorted octahedron (see Table 1). Na and Cd occupy the *A* sites and are coordinated by eight F ions.

Bond valence sums for $NaCdZn_2F_7$ and the known isotypic compounds are given in Table 2. For the *A* sites, a relation of the monovalent to the divalent cation of 1:1 was assumed for these calculations, leading to an ideal bond valence sum of 1.5 for these sites. As can be seen, the resulting values are comparable for $NaCdZn_2F_7$ and $NaCaMg_2F_7$. In both compounds, the divalent cation on the *A* site is significantly 'underbonded', while all other ions show bond valence sums close to the ideal values. In the Sr-containing compound, on the other hand, the divalent cation has a bond valence sum that is slightly too large and the F1 site is strongly 'overbonded'.

None of the structural parameters obtained from the refinement indicates additional ordering of Na and Cd. The refinement of the occupation parameters of Na/Cd did not lead to a considerable deviation from the ideal ratio [refined values $Na_{occ} = 0.4928$ (14) and $Cd_{occ} = 0.5071$ (14)]. In the final refinement, we therefore assumed the ideal occupation parameters ($Na_{occ} = 0.5$ and $Cd_{occ} = 0.5$). To test for the existence of vacancies in the fluorine positions, we also refined the occupation parameters of these positions; yet again this did not result in a significant deviation from the ideal composition. The difference Fourier maps also did not suggest the presence of any fluorine in interstitial sites. All this indicates that the compound is stoichiometric.

In addition, detailed inspection of the reconstructed reciprocal space based on the imaging-plate data does not suggest any further ordering effects, as no traces of diffuse intensities could be detected. We are therefore confident that the distribution of Na and Cd over the two symmetrically independent *A* sites is perfectly random.

Experimental

A crystal of $NaCdZn_2F_7$ was grown from a stochiometric melt using the Czochralski method. Diffraction intensities of a suitable fragment of this crystal were measured at the ANKA-SCD beamline at the Institute for Synchrotron Radiation, Forschungszentrum Karlsruhe, Germany, using a Stoe IPDS II diffractometer ($\lambda = 0.80$ Å), and the same specimen was measured at beamline 'D3' at the Hamburger Synchrotronstrahlungslabor, DESY, Hamburg, Germany, using a four-circle diffractometer equipped with a scintillation counter ($\lambda = 0.45$ Å). For powder diffraction, another fragment of the same crystal was ground. The cubic lattice parameter used in this analysis was determined on the basis of a LeBail fit of synchrotron powder diffraction data measured on the 'Diffraction' beamline in Karlsruhe. The measurements were carried out in the Bragg–Brentano geometry ($\lambda = 0.953$ Å) with an angular step of 0.002°. The measurement was repeated twice to obtain better counting statistics. The data were normalized with the monitor counting rates. Scintillation counter measurements at Hasylab were carried out assuming an *F*-centred cell. Both single-crystal diffractometer measurements confirmed the existence of *d* glide planes, leading to the possible space groups $Fd\bar{3}m$ or $Fd3$ of the cubic or $Fddd$ of the orthorhombic system.

Crystal data

$NaCdZn_2F_7$
$M_r = 399.13$
Cubic, $Fd\bar{3}m$
$a = 10.34657$ (3) Å
$V = 1107.62$ (1) Å^3
$Z = 8$
$D_x = 4.786$ Mg m^{-3}
Synchrotron radiation
$\lambda = 0.45$ Å
Cell parameters from 67 reflections
$\theta = 3$–$35.0°$
$\mu = 8.90$ mm^{-1}
$T = 293$ (2) K
Irregular fragment, colourless
$0.06 \times 0.04 \times 0.01$ mm

Data collection

Huber four-circle four-circle diffractometer (Beamline D3)
ω scans
Absorption correction: numerical (*JANA2000*; Petříček & Dušek, 2000)
$T_{min} = 0.265$, $T_{max} = 0.497$
8160 measured reflections
404 independent reflections
324 reflections with $I > 3\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 31.8°$
$h = -7 \rightarrow 24$
$k = -24 \rightarrow 24$
$l = -24 \rightarrow 23$
2 standard reflections
frequency: 45 min
intensity decay: none

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.039$
$S = 2.30$
404 reflections
11 parameters
$w = 1/[\sigma^2(F_o) + (0.01F_o)^2]$
$(\Delta/\sigma)_{max} = -0.014$
$\Delta\rho_{max} = 3.97$ e Å^{-3}
$\Delta\rho_{min} = -1.18$ e Å^{-3}
Extinction correction: Gaussian Type I (Becker & Coppens, 1974)
Extinction coefficient: 0.21 (2)

Acta Cryst. (2005). E**61**, i182–i184 Friese *et al.* • $NaCdZn_2F_7$ **i183**

Table 1
Selected geometric parameters (Å, °).

Na—F1	2.2401	F1—F2^{i}	3.0233 (13)
Na—F2^{i}	2.5176 (9)	F2—F2^{iii}	2.6593 (3)
Zn—F2^{ii}	2.0197 (5)	F2—F2^{iv}	3.0406 (13)
F1—Na—F1^{v}	180	F2^{ii}—Zn—F2^{ix}	180
F1—Na—F2^{vi}	78.67 (2)	F2^{ii}—Zn—F2^{x}	82.35 (3)
F1—Na—F2^{i}	101.33 (2)	F2^{ii}—Zn—F2^{xi}	97.65 (3)
F2^{i}—Na—F2^{vii}	63.75 (1)	Zn^{xii}—F2—Zn^{xiii}	129.80 (6)
F2^{i}—Na—F2^{viii}	116.25 (1)		

Symmetry codes: (i) $-y, x-\frac{1}{4}, z-\frac{1}{4}$; (ii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (iii) $\frac{1}{2}-z, -x, \frac{1}{2}-y$; (iv) $x, \frac{3}{4}-z, \frac{3}{4}-y$; (v) $-x, -y, -z$; (vi) $y, \frac{1}{4}-x, \frac{1}{4}-z$; (vii) $x, \frac{1}{4}-z, \frac{1}{4}-y$; (viii) $-x, z-\frac{1}{4}, y-\frac{1}{4}$; (ix) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (x) $1-z, \frac{1}{2}-x, \frac{1}{2}-y$; (xi) $z, \frac{1}{2}+x, \frac{1}{2}+y$; (xii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (xiii) $\frac{3}{4}-x, \frac{3}{4}-y, z$.

Table 2
Bond valence sums calculated using the parameters of Brese & O'Keeffe (1991) for $NaCdZn_2F_7$, $NaCaMg_2F_7$ (Oliveira *et al.*, 2004) and $NaSrMg_2F_7$ (Kubel & Dundjerski, 2001).

Numbers in parentheses refer to calculated bond valence sums assuming that the *A* site is occupied by the mono- or divalent cation only.

Atom	$NaCdZn_2F_7$	$NaCaMg_2F_7$	$NaSrMg_2F_7$
A (Na,Cd/Ca/Sr)	1.28 (1.05, 1.51)	1.34 (1.05, 1.63)	1.56 (0.88, 2.23)
B (Zn/Mg)	2.04	2.05	1.98
F1	1.06	1.18	1.46
F2	0.96	0.93	0.93

All three space groups in accordance with the observed extinction rules ($Fd\overline{3}m$, $Fd3$ and $Fddd$; including the corresponding twin models) were tried for refinement. None of the results led to significantly better agreement factors than the ones obtained in the highest-symmetry space group $Fd\overline{3}m$, which we therefore assumed to be the correct choice. Structure refinement was carried out separately with the data sets measured at the two different synchrotron beamlines. The refined parameters show no significant differences. However, as the data set with the scintillation counter was measured up to higher diffraction angles, the precision of the final model is higher. The maximum in the final difference Fourier synthesis is at 0.002 Å from Na/Cd, the minimum is coincident with F1.

Data collection: *DIF4* (Eichhorn & Lippmann, 2001); cell refinement: LeBail fit of synchrotron powder data (*JANA2000*; Petříček & Dušek, 2000); data reduction: *REDUCE* (Eichhorn, 1995) and *AVSORT* (Eichhorn, 1992); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *JANA2000*; molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *JANA2000*.

This work was supported by the European Community – Research Infrastructure Action under the FP6 'Structuring the European Research Area' Programme (through the Integrated Infrastructure Initiative 'Integrating Activity on Synchrotron and Free Electron Laser Science' (IA-SFS RII3-CT-2004-506008). In addition, KF and AG gratefully acknowledge financial support by the Ministerio de Educación y Cultura, Spain.

References

Abrahams, S. C., Marsh, P. & Ravez, J. (1983). *Acta Cryst.* C**39**, 680–683.

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* A**30**, 129–147.

Ben Amara, M., Vlasse, M., Olazcuaga, R. & Le Flem, G. (1979). *Acta Cryst.* B**35**, 50–52.

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.

Dowty, E. (1999). *ATOMS.* Version 5.0.7. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Eichhorn, K. (1992). *AVSORT.* Version 4.2. Hasylab/DESY, Hamburg, Germany.

Eichhorn, K. (1995). *REDUCE.* Version 5.0. Hasylab/DESY, Hamburg, Germany.

Eichhorn, K. & Lippmann, T. (2001). *DIF4.* Hasylab/DESY, Hamburg, Germany.

El Ammari, L., Azrour, M., Depmeier, W., Hesse, K.-F. & Elouadi, B. (1999). *Acta Cryst.* C**55**, 1743–1746.

Friese, K., Gesland, J.-Y. & Grzechnik, A. (2005). *Z. Kristallogr.* **220**, 614–621.

Hund, F. & Lieck, K. (1952). *Z. Anorg. Allg. Chem.* **271**, 17–28.

Ivanov, Yu. A., Simonov, M. A. & Belov, N. V. (1976). *Dokl. Akad. Nauk SSSR*, **228**, 600–602.

Kissel, D. & Hoppe, R. (1988). *Z. Anorg. Allg. Chem.* **557**, 161–170.

Koch, J. & Hebecker, C. (1992). *Z. Anorg. Allg. Chem.* **607**, 121–123.

Kubel, F. & Dundjerski, B. (2001). *Z. Anorg. Allg. Chem.* **627**, 1589–1592.

Oliveira, E. A., Guedes, I., Ayala, A. P., Gesland, J.-Y., Ellena, J., Moreira, R. L. & Grimsditch, M. (2004). *J. Solid State Chem.* **177**, 2943–2950.

Petříček, V. & Dušek, M. (2000). *JANA2000.* Institute of Physics, Academy of the Czech Republic, Prague, Czech Republic.

i184 Friese *et al.* • $NaCdZn_2F_7$ *Acta Cryst.* (2005). E**61**, i182–i184