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The Layered Perovskite $K_2Nd_2Ti_3O_{10}$

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Abstract

Single crystals of dipotassium dineodymium trititanium decaoxide, $K_2Nd_2Ti_3O_{10}$, have been obtained by the flux growth method. The structure is of the Ruddlesden–Popper type and can be described as being composed of blocks of triple perovskite layers separated by rock salt layers.

Comment

In general, there has been interest in members of the $A_2Ln_2Ti_3O_{10}$ series of compounds, where $A = Na, K$ or Rb and $Ln =$ rare earth ion. These compounds are known to exhibit ion exchange and intercalation reactions. In addition, they readily undergo protonation on treatment with dilute acids, making them potentially useful in catalysis and electrochemistry (Richard *et al.*, 1994; Gondrand & Joubert, 1987; Gopalakrishnan & Bhat, 1987).

To date, members of this series have only been isolated in the polycrystalline phase, with principal structural determinations carried out by the use of X-ray powder diffraction. Notably, for the case where $A = K$ and $Ln = Nd$, only the cell constants and space group have been reported (Richard *et al.*, 1994). In this paper, we report the preparation of single crystals of $K_2Nd_2Ti_3O_{10}$, and its structural determination by single-crystal X-ray diffraction.

The structure is described as $I4/mmm$, and the cell parameters obtained are in agreement with those reported for the polycrystalline phase (Richard *et al.*, 1994). It is related to the Ruddlesden–Popper phases $A_4Ti_3O_{10}$ ($A = Sr, Ca$), in that it is composed of triple blocks of corner-shared perovskite layers intergrown with individual rock salt layers (Ruddlesden & Popper, 1958) (Fig. 1). There are two very interesting structural features present in $K_2Nd_2Ti_3O_{10}$. First, we observe in Fig. 1 a marked anisotropy in the displacement parameters of all the O atoms. For O1 and O3, the ellipsoid principal axes are parallel to the c axis, while for O2, in particular, and O4, it lies in the ab plane. In addition, the O1 site exhibits strong

disorder. Initially, O1 was assigned to the $4c$ site, but an extremely high isotropic displacement parameter resulted. Consequently, this site was split by moving to the $8j$ position. These features can be explained by noting that these atoms coordinate the Nd^{3+} ion, which is much smaller than the ions, such as Sr^{2+} , which normally occupy the perovskite A -site in the Ruddlesden–Popper phases. In perovskite materials such as $NdTiO_3$, the Ti–O octahedra exhibit a coherent cooperative tilting to accommodate the smaller Nd^{3+} ion, lowering the symmetry from $Pm3m$ to $Pnma$ (Maclean *et al.*, 1979). However, in the case of $K_2Nd_2Ti_3O_{10}$, the requirement for intergrowth between the perovskite and rock salt layers with dissimilar cations may inhibit coherent cooperative tilting.

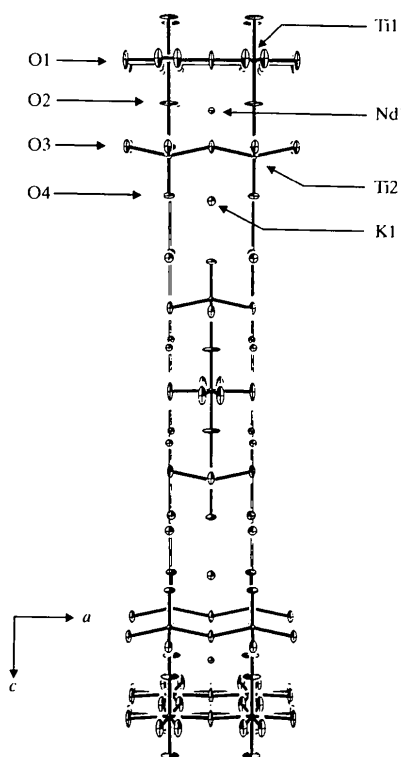


Fig. 1. View of the unit cell of $K_2Nd_2Ti_3O_{10}$ along $[010]$, showing the local Ti2–O octahedron distortion. Displacement ellipsoids are plotted at the 50% probability level.

This case can be contrasted with the classic Ruddlesden–Popper phase $Sr_4Ti_3O_{10}$, as well as with $Ca_4Ti_3O_{10}$. For $Sr_4Ti_3O_{10}$, the structure is tetragonal and described as $I4/mmm$, representing the case where no octahedral tilting is observed. However, substitution of the smaller Ca^{2+} cation in both the perovskite and rock salt layers, as in $Ca_4Ti_3O_{10}$, induces a cooperative

coherent tilting in the octahedral network, such that a lowering of symmetry to orthorhombic *Pcab* is observed (Elcombe *et al.*, 1991). An attempt was made to refine the data for K₂Nd₂Ti₃O₁₀ using this model, but this proved to be unsuccessful. The compound K₂Nd₂Ti₃O₁₀ thus appears to represent an intermediate case, where the octahedral tilting appears to be disordered or incoherent in nature, as shown by the strongly anisotropic O-atom displacement parameters, such that the *I4/mmm* symmetry is preserved.

The second remarkable feature is a local distortion in the Ti2–O octahedron, which is closest to the rock salt layer. The distortion arises when the Ti⁴⁺ cation is displaced from the centre of the coordination sphere towards the rock salt layer. Such distortions are not uncommon for Ti⁴⁺ compounds, *e.g.* BaTiO₃. A rationale for explaining such distortions is based on the nature of the bond network as well as on electronic effects (Kunz & Brown, 1995). For our particular case, a bond valence analysis (Brown, 1992) of the ideal undistorted bond network was carried out, and it was found that the O4 atom is severely underbonded, with only 1.22 valence units. Consequently, it is presumed that the Ti⁴⁺ cation moves off-centre in the coordination sphere to compensate for the deficiency of electronic charge at this site. The end result is a distorted octahedron with an unusually strong Ti2–O4 bond [1.734 (5) Å] and a very weakened Ti2–O2 bond [2.291 (6) Å].

Experimental

Single crystals of K₂Nd₂Ti₃O₁₀ were obtained by the flux method, in which a potassium fluoride/sodium tetraborate flux was used. 0.989 g of pre-fired Nd₂O₃ (99.99% Rhone Poulenc), 1.124 g of TiO₂ (99.999% CERAC), 8.711 g KF (99.999% CERAC) and 1.662 g Na₂B₄O₇ (99.99% Fisher Scientific) were ground together in an inert atmosphere. The reagents were placed and sealed in a 20 ml platinum crucible. The growth conditions involved heating the crucible to 1373 K at 110 K h⁻¹, holding it at this temperature for 2 h, and then cooling to 1273 K at a rate of 1 K h⁻¹. On reaching 1273 K, the crucible was quenched, hot poured and allowed to cool to room temperature. The crystals were obtained as transparent light purple blocks varying from 0.25 to 0.75 mm² in area, each consisting of very thin plates several microns thick. The presence of the metal ions was confirmed by EDAX.

Crystal data

K₂Nd₂Ti₃O₁₀

M_r = 670.38

Tetragonal

I4/mmm

a = 3.8588 (1) Å

c = 29.6561 (7) Å

V = 441.59 (2) Å³

Z = 2

D_x = 5.042 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 4039 reflections

θ = 5.67–38.57°

μ = 15.129 mm⁻¹

T = 300 (2) K

Thin plate

0.356 × 0.194 × 0.006 mm

Colourless

Data collection

Siemens *P4* diffractometer

with a Siemens SMART

1 K CCD area detector

Area detector scans

Absorption correction:

analytical (Sheldrick,

1996)

T_{min} = 0.114, *T_{max}* = 0.912

4977 measured reflections

437 independent reflections

416 reflections with

I > -3σ(*I*)

R_{int} = 0.072

θ_{max} = 38.57°

h = 0 → 4

k = 0 → 6

l = 0 → 51

Intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.026

w*R*(*F*²) = 0.067

S = 1.129

436 reflections

26 parameters

w = 1/[σ²(*F_o*²) + (0.0315*P*)² + 4.0449*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 1.883 e Å⁻³

Δρ_{min} = -2.801 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Nd1	1/2	1/2	0.07246 (1)	0.00971 (10)
Ti1	0	0	0	0.0054 (2)
Ti2	0	0	0.14066 (3)	0.0059 (2)
K1	1/2	1/2	0.20832 (6)	0.0169 (3)
O1†	1/2	0.111 (2)	0	0.030 (2)
O2	0	0	0.0634 (2)	0.051 (3)
O3	0	1/2	0.1269 (2)	0.0176 (7)
O4	0	0	0.1991 (2)	0.0202 (11)

† Site occupancy = 0.5.

The results reported are those for which the O1 atom has been split, with 0.5 occupancy on each site. In addition, the residual electron density Δρ of 1.883 e Å⁻³ is closest to Nd1 at a distance of 0.66 Å.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL93* (Sheldrick, 1993*a*). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993*b*). Molecular graphics: *XP* in *SHELXL93*. Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1188). Services for accessing these data are described at the back of the journal.

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Na₃Mn₄Te₂O₁₂

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Abstract

The title compound, sodium manganese tellurate, was obtained by hydrothermal synthesis and adopts a superstructure related to the CaFe₂O₄ structure type, with the Mn and Te atoms ordered along the *b* axis (short axis in the CaFe₂O₄ structure). Electron-counting schemes show that this compound is a mixed-valence Mn^{II}/Mn^{III} compound, and bond valence sums are used to suggest that there is no site preference for the higher charged Mn atom.

Comment

There are a variety of AB₂X₄ compounds that adopt the CaFe₂O₄ structure type (Decker & Kasper, 1957). Some typical metal oxides include CaCr₂O₄ (Hörkner & Müller-Buschbaum, 1976), CaV₂O₄ (Bertaut *et al.*, 1955) and NaTi₂O₄ (Akimoto & Takei, 1989). Many rare earth sulfides, such as BaSm₂S₄ (Carpenter & Hwu, 1992), also crystallize with this structure type. There are also several cases where the *B* site is populated by several types of atoms, most notably in NaScMO₄ (*M* = Ti, Zr, Hf, Sn) (Reid *et al.*, 1968). In these compounds, there is a random distribution of Sc atoms and the tetravalent metal in the *B* sites. Upon determination of the structure of Na₃Mn₄Te₂O₁₂, we have found, to the best of our knowledge, the first compound that adopts a superstructure of the CaFe₂O₄ structure type, with the

unit cell tripled as a result of the ordering of the Mn and Te atoms along the *b* axis. Columns are made up of repeating groups of edge-sharing octahedra along the *b* axis. These columns have a repeat sequence of MnO₆–TeO₆–MnO₆, and are linked to one another through shared vertices, forming channels that contain the Na atoms. A typical repeating group is shown in Fig. 1, and a polyhedral view of the unit cell of the title compound is shown in Fig. 2.

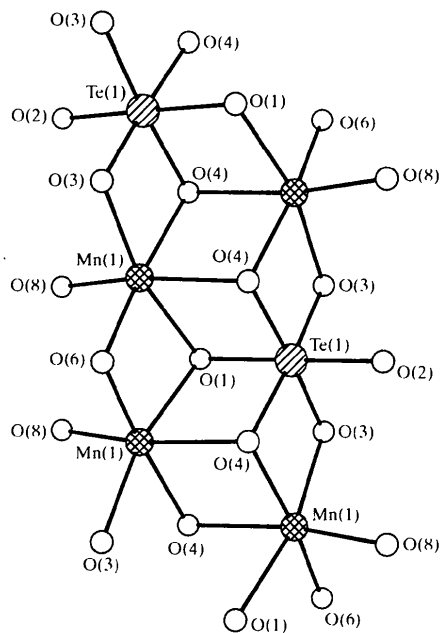


Fig. 1. The repeat sequence of edge-sharing octahedra.

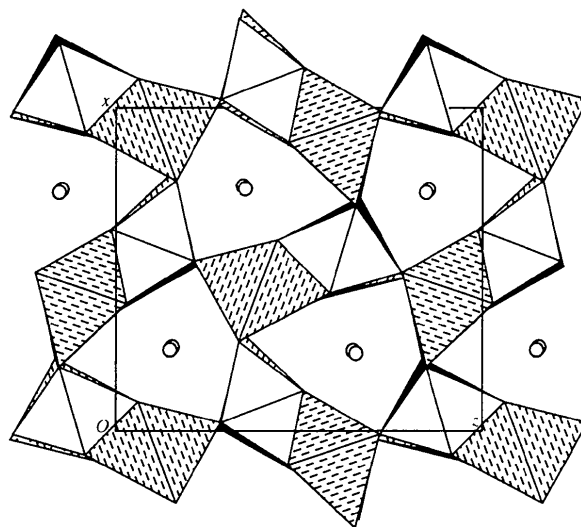


Fig. 2. Polyhedral representation of Na₃Mn₄Te₂O₁₂ viewed down the *b* axis. MnO₆ octahedra are dashed and TeO₆ octahedra are blank. The isolated spheres are Na atoms. The edge-sharing pairs of octahedra at the origin and center of the unit cell contain the Mn(2) and Te(2) atoms. The pairs that contain the Mn(1) and Te(1) atoms are located at (0, *y*, ½) and (½, *y*, 0).