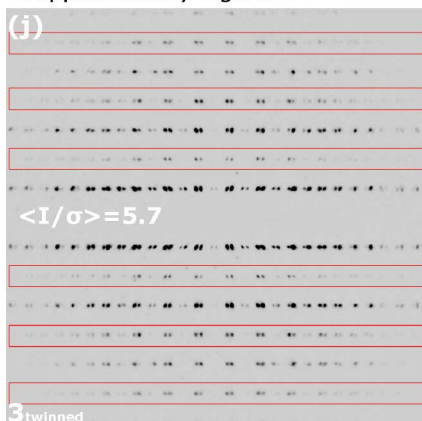
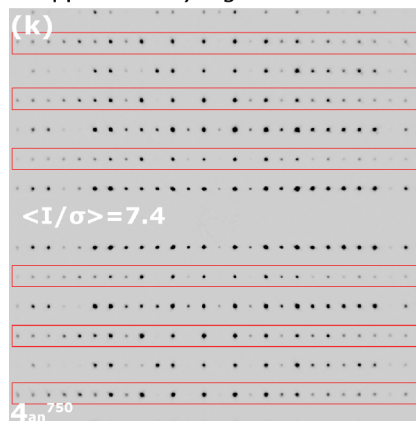


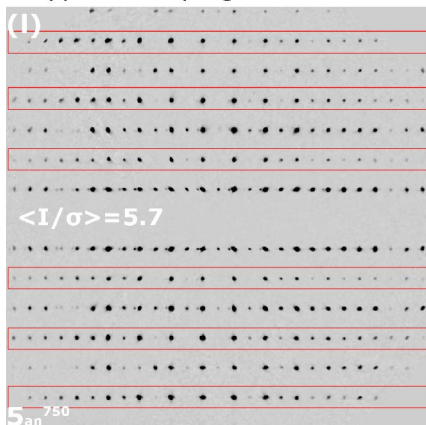
Supplementary Figure 1



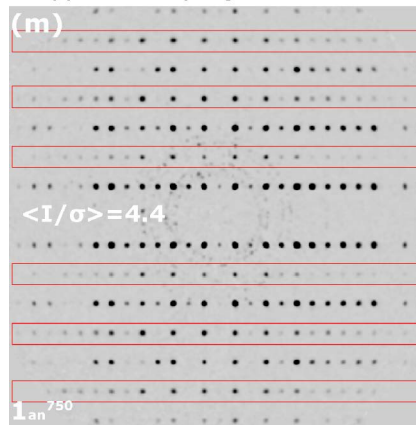
Supplementary Figure 1



Supplementary Figure 1



Supplementary Figure 1



SUPPLEMENTAL FIGURE S1. Precession images of X-ray experiments for studied crystals. $\langle I/\sigma \rangle$ stands for the mean intensity to noise ratio of the reflections breaking C centring of the unit cell (enclosed in red rectangle). Crystal numbers in lower left corner correspond to the names from Table 3.

CONSTRUCTION OF A BÄRNIGHAUSEN TREE

$P2_1/a$ is a subgroup of the $C2/m$ space group. An analysis of symmetry shows that the $P2_1/a$ structure of Nb-rich chevkinite-(Ce) is a distortion derivative (hettotype) (Nespolo 2008) of $C2/m$, the parent structure (aristotype). Transformation occurs by the suppression of a set of symmetry operations of the parent structure (of higher symmetry). It is unambiguous as to which Wyckoff positions are split into two, or more, independent sites. As a result, there are more atoms in the asymmetric unit of the transformed crystal structure. The k2 symbol stands for the class and index of a transformation. Here the hettotype lost a translational symmetry (mirror plane), and belongs to the same crystal class (k from *klassengleiche*) as the aristotype. The primitive cell of the hettotype is twice as large (index 2). The **c**, **b**, **a** and **c-b**, **a** give the new unitary cell vectors order, and $[\frac{1}{2}, 0, \frac{1}{2}]$ is the shift in the origin of the unit cell. Each box on the Bärnighausen tree includes an atom name, Wyckoff symbol with the multiplicity of the site, site symmetry and atom coordinates. The numbers above the arrows are the atom displacements (in Å). The O(1), O(5) and O(8) atoms are split into two symmetrically independent positions (due to a loss of the mirror plane) into O(1) and O(1A), O(5) and O(5A), O(8) and O(8A), respectively.

The $A(1)$ and $A(2)$ sites together with O(3) and O(4) atoms are placed on a mirror plane in the aristotype, which is lost in the hettotype. Atoms released from this plane gain an additional degree of freedom. The largest shift of atoms is expected here, especially for the lighter oxygen atoms. It is indeed the highest, and for crystal 1 reaches 0.22 Å for O(4) and O(3) atoms (Fig. 4). The parameters representing the O(3) and O(4) oxygen atoms can serve as an additional indicator for the identification of the space group. The isotropic displacement parameters (U_{eq}) values hold information on the thermal smearing of atoms and are stored in the cif files containing the details of the X-ray crystal structure. A comparison of these parameters refined first in $C2/m$ and then in $P2_1/a$ against structure factors from one X-ray experiment is needed. If $U_{eq}^{P2_1/a} \approx U_{eq}^{C2/m}$ for a particular atom, the higher symmetry space group (here $C2/m$) is sufficient to define the symmetry of the crystal and should be chosen. If on the other hand the $U_{eq}^{P2_1/a} < U_{eq}^{C2/m}$, the $U_{eq}^{C2/m}$ is enlarged to balance the constraint put on an atom by a symmetry element that actually should not exist (mirror plane in this example) and thus the $P2_1/a$ symmetry for the crystal is correct. For example

in natural crystal 1: $U_{eq}^{O(3)_{C2/m}} = 0.046(2)$; $U_{eq}^{O(3)_{P2_1/a}} = 0.045(2)$; $U_{eq}^{O(4)_{C2/m}} = 0.055(3)$; $U_{eq}^{O(4)_{P2_1/a}} = 0.053(3)$, thus the $C2/m$ space group is a sufficient approximation to the crystal symmetry.

Popov et al. (2001) identified the coordination number (CN) for the $A(1)$ and $A(2)$ sites as 8 and 10 respectively, with the largest A-O contact of 2.997(3) Å. The quality of the X-ray data for Nb-rich chevkinite-(Ce) makes it impossible to determine the bond critical points (Bader 1994, 1998) reliably, which would unambiguously define the $A \dots O$ bonded interactions. Applying, however, an arbitrary distance of ca. 3 Å as a limit enables a determination of a first oxygen shell of these sites. The largest shift of O(3) and O(4) atoms affects this oxygen environment of $A(1)$ and $A(2)$ sites. The number of oxygen atoms within the $A(2)$ O_x shell changes depending on the space group used. For $C2/m$ $A(2)O_{10}$ and for $P2_1/a$ $A(2)O_9$ polyhedra can be defined (when using the same X-ray dataset of natural crystal 1 in both choices).

To demonstrate changes of the AO_x environment due to actual transformation, and at the same time to ensure the presence of $A \dots O$ interaction, we adopted a more restrictive borderline of 2.8 Å for the definition of AO_x shell in these studies. Having these assumptions, we get the $A(2)O_8$ polyhedron with the mean bond length of 2.59(2) for natural ($C2/m$) and $A(2)O_9$ with $\langle A(2)-O \rangle = 2.60(1)$ for transformed, annealed $P2_1/a$ crystal structure.

An analysis of the BO_6 coordination octahedra volume can be another guideline in the determination of the space group of chevkinite crystals. All the transformed $P2_1/a$ crystal structures of Nb-rich chevkinite-(Ce) are characterized by a volume of ca. 12.6 Å³ for the BO_6 octahedra, and of ca. 12 Å³ for natural $C2/m$ structures. This is also true for most other known chevkinites (Haggerty and Mariano 1983; Popov et al. 2001; Sokolova et al. 2004; Xu et al. 2008). The exception is Fe-rich chevkinite-(Ce) (Yang et al. 2007), where the presence of the C centring extinction rule was verified with electron diffraction and X-rays by the authors. The crystal studied there may be on the borderline of a transformation. We have encountered a possibly similar case for crystal 9 annealed at 600 °C for which the $\langle I/\sigma \rangle$ of reflections violating the C centring is equal to 2 (Fig. S1), with, however, a significantly different BO_6 volume (12.6 Å³) than the natural, unannealed crystal 9. On the other hand natural crystal 8 has also $\langle I/\sigma \rangle = 2$ (Fig. S1) for the reflections violating the C centring and its BO_6 volume is still 12 Å³.