



On the crystal structures of Ln_3MO_7 ($Ln = Nd, Sm, Y$ and $M = Sb, Ta$)—Rietveld refinement using X-ray powder diffraction data

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ABSTRACT

We have investigated, using X-ray powder diffraction data, the crystal structures of some fluorite derivatives with the formula Ln_3MO_7 ($Ln =$ lanthanide or Y and $M = Sb$ and Ta). In these compounds ordering of Ln and M occurs, leading to a parent structure in $Cmmm$. Tilting of the MO_6 octahedra causes doubling of one of the cubic axes, leading to a number of non-isomorphic subgroups, e.g. $Cmcm$, $Ccmm$ and $Cccm$. We have identified an alternative space group $Ccmm$ instead of $C22_1$ for those compounds containing a medium sized lanthanide or Y and M being Sb or Ta. Interestingly this is an alternative setting for the space group of the structure obtained when Ln is large ($Cmcm$). However, there tilting of the octahedra is around the a -axis of the parent structure, rather than around the b -axis as it is found in the compounds which we are reporting on here.

In one compound, Nd_3TaO_7 , both tilts occur. The phase transition between the two possible structures is a slow and difficult process above 80K, allowing both phases to coexist.

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1. Introduction

A large number of compounds with the general formula Ln_3MO_7 , in which Ln is a trivalent lanthanide or Y and M is a pentavalent metal cation, adopt a structure related to the defect-fluorite. Allpress and Rossell [1,2] have initially studied the compounds with $M = Nb, Ta$ and Sb , and proposed three types of crystal structures. The first type crystallizes in the space group $Cmcm$ which is found in compounds containing large lanthanides. The second one has the space group $C22_1$, a subgroup of $Cmcm$, which is adopted by lanthanides with a medium size including Y. For even smaller lanthanides, the cubic defect fluorite structure is generally observed.

The most interesting structural feature of the first two types is the ordering of Ln and M cations with the ratio of 3:1. This cation ordering together with the anion ordering of the oxygen vacancies lead to the corner-shared MO_6 octahedra forming one-dimensional chains parallel to the [001] direction of the orthorhombic structure. The main difference between the two structures is, however, the tilting of the MO_6 octahedra being around the axes either parallel to [100] (in $Cmcm$) or to [010] (in $C22_1$), respectively.

In the past years, the structural, electronic and magnetic properties of several Ln_3MO_7 compounds, with $Ln =$ lanthanide or

$Y, M = Nb, Ta, Mo, Re, Ru, Os, Ir$ and Sb , have been investigated because of their interesting one-dimensional structural property [1–18]. The existence of the first type of structure (space group $Cmcm$) has been confirmed by neutron powder diffraction [4,8,10,11], X-ray powder diffraction [2,5,7,14,15,17] as well as by X-ray single crystal diffraction [13]. Of the second type, only limited X-ray powder diffraction studies were reported. Rossell [2] determined the structure of Y_3TaO_7 and reported the space group $C22_1$. According to Allpress and Rossell [1] Y_3SbO_7 has the same structure. Recently studies have been published on the compounds Ln_3TaO_7 [5], Dy_3ReO_7 [7] and Eu_3NbO_7 [18]. However, from the refined atomic positions given in these studies, one notices that some shifts of metal atoms from the ideal position are statistically not significant. In addition, the geometry of the MO_6 described in $C22_1$ does not correspond to a tilt of the rigid octahedron: the basal oxygen atoms are not co-planar and the O–O distances of the opposite edges are either too short (e.g. $d_{O_2-O_2} = 2.35 \text{ \AA}$ in Y_3TaO_7) or too long ($d_{O_1-O_1} = 3.03 \text{ \AA}$) [2]. These facts may suggest an inappropriate choice of space group. Furthermore, the transition from the $Cmcm$ structure to that of the $C22_1$ has been observed in Nd_3TaO_7 [5].

In continuation of our recent works on the weberite-like $Ca_2Ln_3Sb_3O_{14}$ [19] and the chiolite-like $Ca_5Te_3O_{14}$ [20], we have re-investigated, using X-ray powder diffraction data, the structures occurring in the fluorite-related compounds Ln_3MO_7 ($Ln =$ lanthanide and Y; $M = Ta$ and Sb) with emphasis on the structures adopted by those of the medium-sized lanthanides. In this paper, we show that the space group $C22_1$ once reported

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in these systems is inappropriate and the correct one is likely to be *Cmcm*. Remarkably, this space group and the unit cell are the same as those observed for large lanthanides but with different tilting direction of the MO_6 octahedra. We have confirmed also that Nd_3TaO_7 occurs in both *Cmcm* and *Ccm* space groups and that the *Cmcm* \rightarrow *Ccm* phase transition is sluggish due to the kinetic factors.

2. Experimental

Samples of Ln_3SbO_7 and Ln_3TaO_7 , with $Ln = Nd, Sm$ and Y , were prepared from Nd_2O_3 , Sm_2O_3 , Y_2O_3 , Sb_2O_3 and Ta_2O_5 in alumina crucibles using the standard solid-state reaction. Nd_2O_3 was heated at 1273 K overnight beforehand. The mixture containing Sb_2O_3 was first heated overnight at 1073 K. After grinding, the resulting powder was sintered for several days at 1473 K. For the Ta compounds the sintering temperature was 1773 K. The syntheses were carried out in air and all samples were furnace cooled to room temperature.

X-ray powder diffraction data were collected on a Philips X'Pert diffractometer, equipped with the X'Celerator, using $CuK\alpha$ radiation. For non-ambient X-ray diffraction, an Anton Paar TTK 450 chamber was used with direct sample cooling/heating in the temperature range between 80 and 723 K and a temperature stability of ~ 0.1 K. The patterns were measured in the 2θ range between 10° and 140° in steps of 0.02° (2θ), counting time 10 s. The model refinements were performed by the Rietveld method using the Rietica computer program [21]. A fifth order polynomial function with six parameters was used to fit the background. The profiles were described by a pseudo-Voigt function.

3. Results

X-ray diffraction patterns of Ln_3MO_7 , $Ln = Sm$ or Y and $M = Ta$ or Sb show a C-centred orthorhombic unit cell with the cell parameters $a \approx 2a_c$, $b \approx \sqrt{2}a_c$, and $c \approx \sqrt{2}a_c$, where a_c is the lattice parameter of the cubic fluorite ($a_c \approx 5.3 \text{ \AA}$). Close inspection of the superlattice reflections (Fig. 1) has revealed the presence of the (201) diffraction line at $2\theta \approx 20.7^\circ$ ruling out the space group *Cmcm* for these compounds. The structure of Ln_3MO_7 with $Ln = Sm$ or Y and $M = Ta$ or Sb was first modelled in the space group *C222*₁, as was reported in the literatures [1,2]. While all refinements did result in a reasonably low R_{wp} -value, the displacements of some metal atoms from the ideal positions in *Cmcm* were found to be insignificant with respect to their standard deviations. In the case of Y_3SbO_7 , for example, the y -coordinate of Y1 is 0.5011(13). Also the refined z -coordinate of Y2 and y -coordinate of Sb are 0.0027(11) and $-0.0051(11)$, respectively. Furthermore, the refinement in *C222*₁ resulted in high values of the correlation between O1 and O2, indicating that they are possibly equivalent. These observations let us to suspect the correctness of *C222*₁ and to consider another space group with higher symmetry. To conserve the typical structure, i.e. the MO_6 octahedra being tilted round the two-fold axes parallel to [010], as well as the observed superlattice reflections, the space group *Ccm* was chosen. To get the origin on the centre of symmetry, shifting the origin along the c -axis by $\frac{1}{4}c$ was necessary. Consequently, the position of the M atoms is moved from the $0, y, \frac{1}{4}$ ($y \approx 0$) in *C222*₁ to a centre of symmetry at 000 in *Ccm*. Also the $Ln1$ atoms are in the centrosymmetric position at $0, \frac{1}{2}, 0$ instead of at $0, y, \frac{1}{4}$ ($y \approx 0.5$). Clearly, the new space group *C2/c2/m2₁/m* is a super group of *C222*₁. The MO_6 octahedron described in *Ccm* is more symmetric.

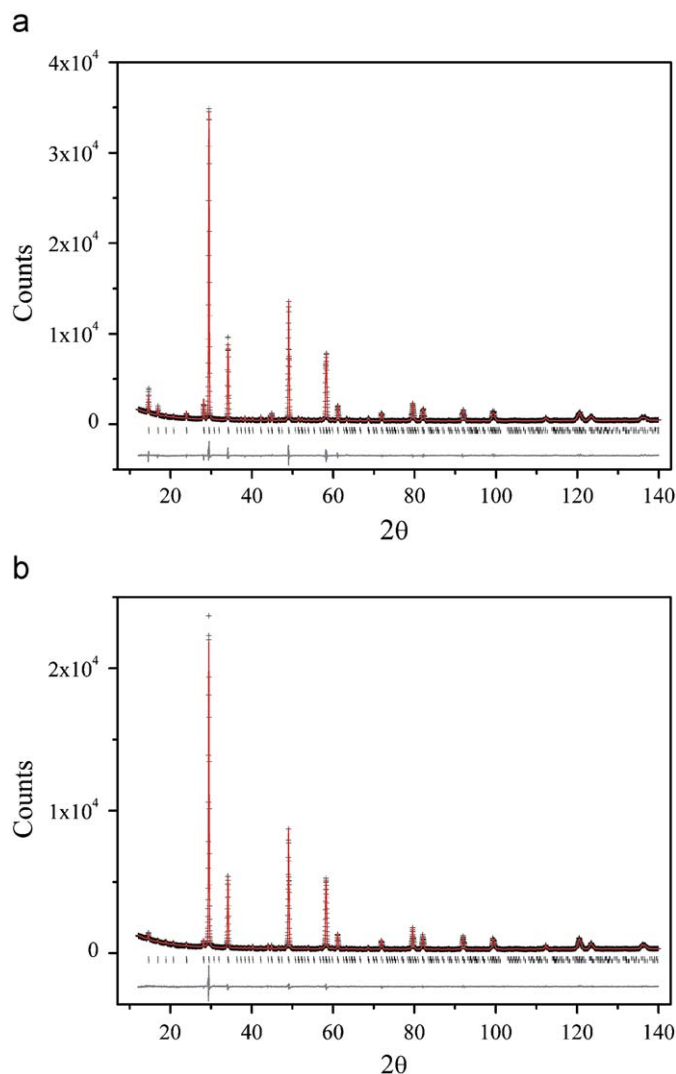


Fig. 1. Observed (crosses) and calculated (full line) profiles of the X-ray powder diffraction for Y_3TaO_7 (a) and Y_3SbO_7 in the space group *Ccm*. Tick marks below the profiles indicate the positions of the allowed Bragg reflections. A difference curve (observed–calculated) is shown at the bottom.

The Rietveld refinements carried out in *Ccm* yielded good matches between the experimental and the calculated data. In particular, the resulted agreement factors (R_{wp}) are the same as those obtained in the space group *C222*₁ despite that the new model has many fewer structural parameters (8 vs. 14). Fig. 1 shows the plots of the observed and calculated profiles for Y_3MO_7 ($M = Ta$ and Sb). The refined lattice parameters and structural parameters are given in Table 1. Table 2 lists some selected interatomic distances.

The structures that occur in Nd_3TaO_7 at non-ambient temperatures were analysed in the same way. The phase transition can be easily seen by inspecting the (400) and (022) reflections. In the *Cmcm* structure these reflections separate largely and they practically merge together to a single line in the case of *Ccm* (see also discussion). In Fig. 2 we plot the evolution of the (400) and (022) reflections as the function of temperature. At room temperature, both *Cmcm* and *Ccm* phases coexist which is in agreement with the observation in the literature [5]. The coexistence of two phases persists till 80 K, the lowest temperature being reachable with the TTK450 chamber. Upon heating, the amount of the *Ccm* phase decreases and it disappears at about above 623 K. The existence of a two phase

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