Journal of Solid State Chemistry 229 (2015) 330–335

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

New rhombohedral pyrochlores $Ca_2Ln_3Sb_3O_{14}$ (Ln=lanthanide and Y): Space group revised

W.T. Fu*, D.J.W. IJdo

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300RA Leiden, The Netherlands

ARTICLE INFO

Article history:
Received 30 April 2015
Received in revised form
4 June 2015
Accepted 5 June 2015
Available online 20 June 2015

Keywords:
Structure determination
Rhombohedral pyrochlore
X-ray diffraction

ABSTRACT

The structure of calcium rare earth antimonates with the formula $Ca_2Ln_3Sb_3O_{14}$ (Ln= lanthanide and Y) has been re-examined by Rietveld refinements using either combined X-ray and neutron diffraction data or X-ray diffraction data alone. Contrary to a previous study reporting the monoclinic structure with the space group $I2/m11$, we found that the correct space group is $R\bar{3}m$. In addition, $Ca_2Ln_3Sb_3O_{14}$ are not weberite-like and belong to the pyrochlore family. The structure resembles that of the recently reported rhombohedral pyrochlores $Mn_2Ln_3Sb_3O_{14}$ but with disordering of Ca and Ln on both A and one of the B positions. These compounds provide thus new examples of rhombohedral pyrochlore that are derived from the cubic pyrochlores by a 1:3 ordering in both A and B sites.

1. Introduction

Oxides with the general formula $A_2B_2O_7$, in which A and B are a large and a small cation respectively, may adopt either the orthorhombic weberite ($Sr_2Sb_2O_7$) [1] or the cubic pyrochlore ($La_2Zr_2O_7$) structure [2]. Both structures can be viewed as anion-deficient fluorite related superstructures. They consist of similar cationic layers with the composition A_3B and AB_3 packed alternatively along the [111] of the parent fluorite. The difference between weberite and pyrochlore is the difference in the relative position between A_3B and AB_3 layers, which results in the space groups $Imma$ and $Fd\bar{3}m$, respectively. Besides the difference in cationic sublattice, the anion sublattice differs from one another. In weberite, all oxygen anions are part of the octahedral BO_6 framework resulting in the $B_2O_7{}^{4-}$ stoichiometry. The two different A-cations are coordinated to eight oxygens: one is in a square prism and the other is in a hexagonal bipyramid. In pyrochlore, on the other hand, the composition of the octahedral framework is $B_2O_6{}^{2-}$; one oxygen atom (O at 8b) coordinates to the atoms of type A only. There is only one type of A-cations coordinating with 8 oxygen atoms in a deformed cubic prism.

The series of compounds with the formula $Ca_2Ln_3Sb_3O_{14}$ (Ln=lanthanide and Y) was first reported by Burchard and Rüdorff [3]. Based on X-ray powder diffraction data, they found a body-centred orthorhombic cell for compounds with larger lanthanides, e.g. Ln= La, Nd, Sm and Gd, and a primitive tetragonal unit cell with smaller Ln, i.e. Dy, Yb, Lu and Y. They suggested that $Ca_2Ln_3Sb_3O_{14}$ are of chiolite-type ($Na_5Al_3F_{14}$) [4], but did not give detailed structural information. Some years ago, we have investigated the crystal structure of $Ca_2Ln_3Sb_3O_{14}$, with Ln=La, Pr, Nd and Y, by the Rietveld method using combined X-ray and neutron powder diffraction data [5]. Since the trial models derived from the chiolite structure could not fit adequately the diffraction data and the reported lattice parameters resemble those of the weberite $Sr_2Sb_2O_7$ [1], we refined the structure of $Ca_2Ln_3Sb_3O_{14}$ in the monoclinic space group $I2/m11$, a subgroup of $Imma$.

There is currently some interest in $Ca_2Ln_3Sb_3O_{14}$. Brik et al. have calculated the electronic structure of $Ca_2La_3Sb_3O_{14}$ and showed existence of a direct band gap of 1.864 eV (generalised gradient approximation) or 2.443 eV (local density approximation) [6]. The luminescent properties of Eu^{3+} and Pr^{3+} in $Ca_2La_3Sb_3O_{14}$ have also been reported by Srivastava et al. [7]. The emission spectrum of Eu^{3+} shows strong lines of the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_2$ transitions which are inconsistent with the assigned space group $I2/m11$ from the crystallographic study [5].

Recently we have reported the preparation and crystal structure of a new series of manganese rare earth antimonates with formula $Mn_2Ln_3Sb_3O_{14}$ (Ln=La–Yb and Y) [8]. The compounds with Ln=La, Pr and Nd crystallise in a rhombohedral supercell of the cubic fluorite with the space group $R\bar{3}m$. The structure is pyrochlore-like but differs from the common cubic pyrochlore $A_2B_2O_7$ in that it consists of fully ordered Mn/Ln in the A sites and Mn/Sb in the B sites with the ratio 1:3. To the best of our knowledge, they are the first examples of rhombohedral pyrochlore oxides. Since the chemical formulae of the two rare earth antimonates are quite similar and the space group $I2/m11$ is actually a

---

* Corresponding author. Fax: +31 71 5274537.
E-mail address: w.fu@chem.leidenuniv.nl (W.T. Fu).

http://dx.doi.org/10.1016/j.jssc.2015.06.013
0022-4596/© 2015 Elsevier Inc. All rights reserved.

subgroup of $R\bar{3}m$, it prompts us to re-examine the crystal structure of $Ca_2Ln_3Sb_3O_{14}$. In this paper we report the revised crystal structure of the title compounds showing that they are new examples of rhombohedral pyrochlore.

2. Experimental

The preparation of $Ca_2Ln_3Sb_3O_{14}$ has been described previously [5]. X-ray powder diffraction data were recorded using a Philips X'Pert diffractometer, equipped with the X'Celerator using Cu Kα1 and Kα2 radiations, in steps of 0.02° (2θ) and 10 s counting time between 10° and 140° (2θ). Neutron powder diffraction data were collected on the powder diffractometer of the Petten High Flux Reactor. A wavelength of 1.4317 Å was used. The calculations were carried out with the Rietica computer programme using either combined neutron and X-ray diffraction data or X-ray diffraction data alone [9]. A 5th order polynomial function with six parameters and a Chebyshev polynomial function with twelve parameters were used to fit the background of neutron and X-ray data respectively. The profiles were fitted using a Gauss function for neutron data and a Pseudo-Voigt function for X-ray data.

3. Results

X-ray diffraction pattern of $Ca_2La_3Sb_3O_{14}$, together with the Mn-analogue for comparison, is shown in Fig. 1. The main diffraction lines resemble those of cubic pyrochlore ($a \approx 10.69$ Å), but the appearance of some weak reflections, e.g. $2\theta \approx 16.5°$ and 37.8°, as well as the peak profiles cannot be explained by the space group $Fd\bar{3}m$. Clearly, the distortion from cubic symmetry in $Ca_2Ln_3Sb_3O_{14}$ is smaller than that of the Mn-analogues; in the later compounds the strongest (222) reflection of cubic pyrochlore ($2\theta \approx 30°$) splits into two separate lines. To find out the true symmetry, we have closely examined some diagnostic reflections of compounds showing large peak splitting at higher 2θ-angles. Fig. 2 shows an enlarged section of the X-ray diffraction pattern of $Ca_2Nd_3Sb_3O_{14}$ containing the cubic (444) ($2\theta \approx 60.5°$) and (800) ($2\theta \approx 71°$) reflections. As can clearly be seen, the (444) reflection splits into a doublet with the intensity ratio of about 3:1 and the (800) reflection remains single. The characteristics of peak splitting of the (*hhh*)- and (*h*00)-type reflections indicate a rhombohedral distortion. For a monoclinic distortion, these peaks would split into triplets and doublets, respectively. To further confirm if the observed profiles are in agreement with the rhombohedral symmetry, we fitted the whole pattern using Le Bail method in the space group $R\bar{3}m$. Le Bail fitting results in a perfect match of profiles for all reflections with the refined lattice parameters (hexagonal setting): $a = 7.50198(4)$ Å and $c = 18.27808(14)$ Å (Fig. 2).

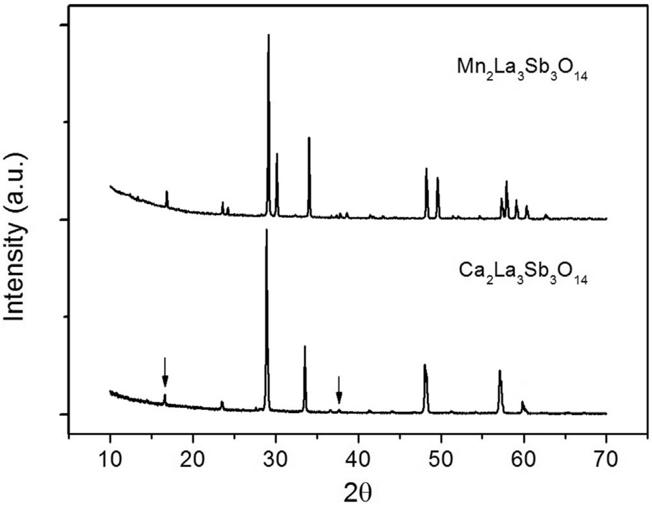

Fig. 1. X-ray diffraction patterns of $Ca_2La_3Sb_3O_{14}$ as compared with $Mn_2La_3Sb_3O_{14}$. Arrows indicate reflections that cannot be indexed with the space group $Fd\bar{3}m$.

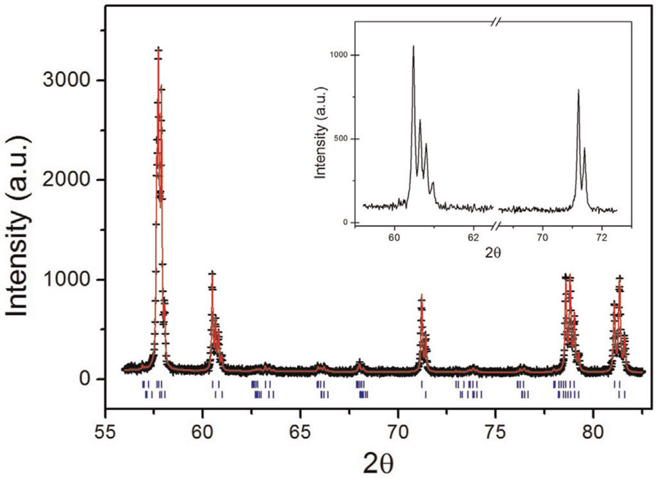

Fig. 2. An enlarged section of the X-ray diffraction pattern of $Ca_2Nd_3Sb_3O_{14}$ with an inset showing the (444) and (800) reflections as indexed with the cubic pyrochlore unit cell. Note that the splitting of the singlet (800) reflection is due to Cu Kα1 and Kα2 radiations. The continuous line (red) is the Le Bail fit using the space group $R\bar{3}m$. The significance of the peak splittings is discussed in the text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The Rietveld refinements were carried out using combined neutron and X-ray diffraction data for Ln = La, Pr, Nd and Y [5]. For other lanthanides, only X-ray diffraction data were used in the refinements. The calculations were first performed in the space group $R\bar{3}m$ with fully ordered arrangement of metal atoms: Ca in 3*a* and 3*b*, Sb and Ln in 9*d* and 9*e*, respectively [8]. Although the refinements went smoothly, the obtained agreement factors are systematically higher than those in the space group $I2/m11$ (R_{wp}: 3.54/14.27% vs. 3.05/11.13% for neutron and X-ray data of $Ca_2La_3Sb_3O_{14}$). In particular, the intensity fit of X-ray data was less than optimal which can be seen in Fig. 3 (upper part). In the next refinements, we considered the possible disordering between Ca and Ln ions as was previously observed in the monoclinic model [5]. The disordered model improves considerably the refinements and yielded good agreement between the experimental and calculated data (see lower part of Fig. 3). The agreement factors are essentially the same as were obtained with the monoclinic model (e.g. R_{wp}: 3.09/10.78% vs. 3.05/11.13% for $Ca_2La_3Sb_3O_{14}$). Considering further that the total refinable atomic position parameters of the rhombohedral model (5 variables) is less than half of that of the monoclinic model (12 variables), the space group $R\bar{3}m$ describes correctly the structure of $Ca_2Ln_3Sb_3O_{14}$.

The refined lattice parameters and the atomic positions are given in Table 1. Fig. 4 shows the plot of the observed and calculated neutron profiles of the compounds with Ln = La and Nd. Some selected interatomic distances and angles are listed in Table 2.

4. Discussion

$Ca_2Ln_3Sb_3O_{14}$ were originally described as chiolite-like compounds probably because the ratio between the large and small cations resembles the mineral chiolite ($Na_5Al_3F_{14}$) [4]. The present