The disordered cubic structure of $Ca_7Co_3Ga_5O_{18}$

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Abstract

The new mixed oxide having composition close to $Ca_7Co_3Ga_5O_{18}$ was synthesized from $CaCO_3$, Co_3O_4 and Ga_2O_3 at 1150 °C in air and studied by neutron and synchrotron X-ray powder diffraction, selected-area electron diffraction and high-resolution electron microscopy. The structure was refined, using time-of-flight (TOF) neutron powder diffraction data, in space group $F432$, with $a = 15.0487(4)$ Å and $Z = 8$, to $R_F = 0.7\%$. It is considerably disordered, with four different tetrahedral sites randomly occupied by Co and Ga atoms at a ratio of 1:2. The tetrahedra form a disordered $(Co_{1/3}Ga_{2/3})O_2$ 3D-framework inside which isolated CoO_6 octahedra, surrounded by 8 Ca atoms, are located. The structure is related to the ordered structure of $Ca_{14}Al_{10}Zn_6O_{35}$. Electron diffraction patterns confirmed the symmetry and unit cell and revealed no diffuse scattering. High-resolution electron microscopy images showed the absence of extended structural defects.

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1. Introduction

The interest in cobalt containing oxides has lately increased due to their potential applications in solid oxide fuel cells and ceramic membranes for high-temperature oxygen separation [1,2]. The desired properties are frequently found for compounds with perovskite-related structures and many investigations are therefore focused on this class of compounds.

During the search of the new compounds with perovskite-related structures in the Ca–Co–Ga–O system we have recently discovered a new compound with a composition close to $Ca_2Co_{0.8}Ga_{1.2}O_{4.8}$. The actual crystal structure of this compound remained unsettled, although its electric transport and magnetic properties were characterized and interpreted [3]. It is a *p*-type semiconductor, with a small polaron conduction me-

chanism and an unusually large mobility activation energy of 0.45 eV, the latter was supposed to be attributed to a large spatial separation of the cobalt ions in the structure. However, nothing was really known about the crystal structure at that stage, which is necessary for a complete understanding of the phase and its physical properties. In this paper, we report the crystal structure for this compound, having the ideal composition $Ca_7Co_3Ga_5O_{18}$ and a disordered variant of the structure of $Ca_{14}Al_{10}Zn_6O_{35}$ ($Ca_7Al_5Zn_3O_{17.5}$) [4].

2. Experimental

Synthesis of different polycrystalline samples in the Ca–Co–Ga–O system was performed in air at 1150 °C using $CaCO_3$, Co_3O_4 and Ga_2O_3 as starting materials. Phase analysis of the products was made by means of their X-ray diffraction (XRD) powder photographs, recorded in a Guinier camera with Cu $K\alpha_1$ radiation and

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Si as internal standard. Time-of-flight (TOF) neutron powder diffraction (NPD) data were collected on the Polaris diffractometer at the UK neutron spallation source ISIS, Rutherford Appleton Laboratory. Synchrotron XRD data were collected on the beamline ID31 at the ESRF, Grenoble. Structure refinements were carried out using the GSAS program [5].

Electron diffraction (ED) studies were carried out using a JEOL JEM 2000 FX transmission electron microscope (TEM), operated at 200 kV, and high-resolution electron microscopy (HREM) studies in a JEOL JEM 3010 instrument, operated at 300 kV. Small amounts of the samples were crushed in n-butanol and a drop of this dispersion was put on a holey carbon film, supported by a copper grid. Micro-analyses of individual crystallites, for the determination of the cation composition, were performed on the same grids that were studied in the TEM, using a JEOL JSM 880 scanning electron microscope equipped with a windowless energy-dispersive X-ray (EDX) LINK Isis analyzer. The program suite MacTempas [6] was used for HREM image simulations.

3. Results

The X-ray and neutron powder patterns indicated that the crystal structure of the cubic phase in the sample with nominal composition $Ca_2Co_{0.8}Ga_{1.2}O_{4.8}$ is

related to that of $Ca_7Al_5Zn_3O_{17.5}$, which crystallizes in the space group $F23$ with $a = 14.868$ Å [4]. Calculated and observed reflection intensities showed, however, a poor fit when using this structure model, and difference Fourier maps showed that additional atomic sites are occupied. Addition of atoms on these sites and refinements of metal site occupancies eventually led to a set of atomic positions that showed that the space group symmetry could be increased to the super-group $F432$. At the end, an idealized structure model was found to yield a good fit with observed intensities. This idealization consisted in (i) adopting a tentative composition $Ca_7(Co, Ga)_8O_{18}$ in the final refinement and (ii) assuming that Co and Ga atoms statistically occupy 4 different tetrahedral sites in equal proportions (Co:Ga = 1:2). The refined structural parameters for this model are given in Table 1. Deviations from this ideal structure model (and composition) are, as assessed below, found to be small. In what follows, an account of the refinements using this idealized model is first given, followed by a description of the structure and then an evaluation of possible structural and compositional deviations from the ideal model.

3.1. Determination and refinement of the structure using powder diffraction data

Three data sets were used to determine and refine the structure: (i) TOF neutron data recorded for a sample

Table 1
Structural parameters refined from TOF-NPD Data (upper values) and synchrotron XRPD data at 10 K (lower values) for $Ca_7Co_3Ga_5O_{18}$

Atom	Site	x	y	z	$U_{eq}*100(\text{Å}^2)$	sof
Ca1	24e	a	0.21119(5)	0	0	1.10	1
		b	0.2106(1)	0	0	1.05	1
Ca2	32f	a	0.38962(3)	0.38962	0.38962	0.82	1
		b	0.38947(6)	0.38947	0.38947	0.73	1
Co	4b	a	1/2	1/2	1/2	0.96	1
		b	1/2	1/2	1/2	0.55	1
MI	4a	a	0	0	0	0.59	1/3Co + 2/3Ga
		b	0	0	0	0.83	1/3Co + 2/3Ga
M2	24d	a	0	1/4	1/4	0.80	1/3Co + 2/3Ga
		b	0	1/4	1/4	0.80	1/3Co + 2/3Ga
M3	32f	a	0.17448(5)	0.17448	0.17448	1.29	0.216(1)Co + 0.432(3)Ga
		b	0.1743(1)	0.1743	0.1743	1.18	0.226(2)Co + 0.452(3)Ga
M4	32f	a	0.1440(1)	0.1440	0.1440	1.37	0.117(1)Co + 0.234(3)Ga
		b	0.1443(2)	0.1443	0.1443	1.15	0.107(2)Co + 0.215(3)Ga
O1	96j	a	0.24483(4)	0.14647(2)	0.07030(3)	1.64	1
		b	0.2448(3)	0.1468(2)	0.0705(2)	0.95	1
O2	8c	a	1/4	1/4	1/4	2.49	1
		b	1/4	1/4	1/4	2.85	1
O3	24e	a	0.36955(4)	0	0	0.72	1
		b	0.3702(3)	0	0	0.84	1
O4	32f	a	0.06974(5)	0.06974	0.06974	1.62	1/2
		b	0.0682(3)	0.0682	0.0682	1.32	1/2

Note: The refined parameters are for the ideal structure model with Co and Ga atoms statistically distributed over the M sites in a 1:2 ratio and the sum of the sof's for sites M3 and M4 equal to 1. Cubic, $a = 15.0487(4)$ Å, $V = 3408.0(1)$ Å^3 (NPD data), $a = 14.99871(4)$ Å, $V = 3374.13(1)$ Å^3 (XRD data), $Z = 8$, $F432$ $a = 15.01364(2)$ Å.

with nominal composition $Ca_{2.00}Co_{0.80}Ga_{1.20}O_{4.8}$ (Ca_{60} $Co_{24}Ga_{36}O_{144}$), (ii) synchrotron X-ray data (recorded at 10 K with $\lambda = 0.50029$ Å) for a sample with nominal composition $Ca_{1.87}Co_{0.87}Ga_{1.27}O_x$ ($Ca_{56}Co_{26}Ga_{38}O_x$— the nominal composition was based on the result from the first stages of the structure determination), and (iii) synchrotron X-ray data for the latter sample recorded at room temperature and using a wavelength $\lambda = 1.6071$ Å, on the high-energy side of the Co K absorption edge at $\lambda = 1.608$ Å.

For the TOF data, the 145° back-scatter bank and the d range 0.5–3.18 Å, containing 772 reflections, were used. The neutrons scattering lengths used were Ca = 0.470, Co = 0.249, Ga = 0.7288, and O = 0.5803×10^{-12} cm [7], and an absorption correction of $\mu R = 0.06$ was applied. Three impurity phases were observed, CaO, CoO and Co_3O_4. They were included in the refinements, with refined lattice parameters and common thermal displacement parameters. A difficulty was encountered with the background, which showed fluctuations at low d-values, below ca. 1.5 Å. The problem was overcome by cyclically refining the background using 36 coefficients for the GSAS background function 8 (linear interpolation in segments of $1/d$) and the other parameters. A total of 59 parameters were used in the final refinement, including 9 positional and 24 anisotropic thermal parameters for $Ca_7Co_3Ga_5O_{18}$. The residual indices were $\chi^2 = 3.02$, $wR_p = 0.9\%$, $R_p = 1.6\%$, $R_I = 1.0\%$, $R_F = 0.7\%$ and $DwD = 0.28$. The refined amounts of the impurity phases were, relative to one mole of $Ca_{56}Co_{24}Ga_{40}O_{144}$, 1.04(4) CaO (0.65(3) wt%, $R_F = 1.5\%$ for 40 reflections), 1.30(4) CoO (1.09(3) wt%, $R_F = 0.3\%$ for 29 reflections) and 0.11(1) Co_3O_4 (0.30(4) wt%, $R_F = 2.0\%$ for 132 reflections). A part of the TOF NPD pattern is shown in Fig. 1.

In the refinement using the synchrotron data recorded at 10 K, the 2θ range 2.5–60° (0.5–11.35 Å) was used, containing 780 reflections, and a total of 70 parameters were refined. The anomalous dispersion coefficients f' and f'' used were for Ca = 0.111, 0.155, for Co = 0.224, 0.515, for Ga = 0.242, 0.871, and for O = 0.001, 0.003 electrons/atom. They were calculated using the GSAS accessory program FPrime. An absorption correction of $\mu R = 2.8$ was applied, calculated for a 0.4 mm radius capillary and a 60% packing density. The residual indices were $\chi^2 = 1.45$, $wR_p = 11.7\%$, $R_p = 9.0\%$, $R_I = 5.3\%$, $R_F = 4.3\%$ and $DwD = 1.56$. The refined amounts of the observed impurity phases, tetragonal CoO and Co_3O_4, were 1.77(7) CoO (1.29(5) wt%, $R_F = 7.6\%$ for 65 reflections) and 0.47(2) Co_3O_4 (1.29(5) wt%, $R_F = 8.6\%$ for 133 reflections). The fit between observed and calculated pattern is shown in Fig. 2a.

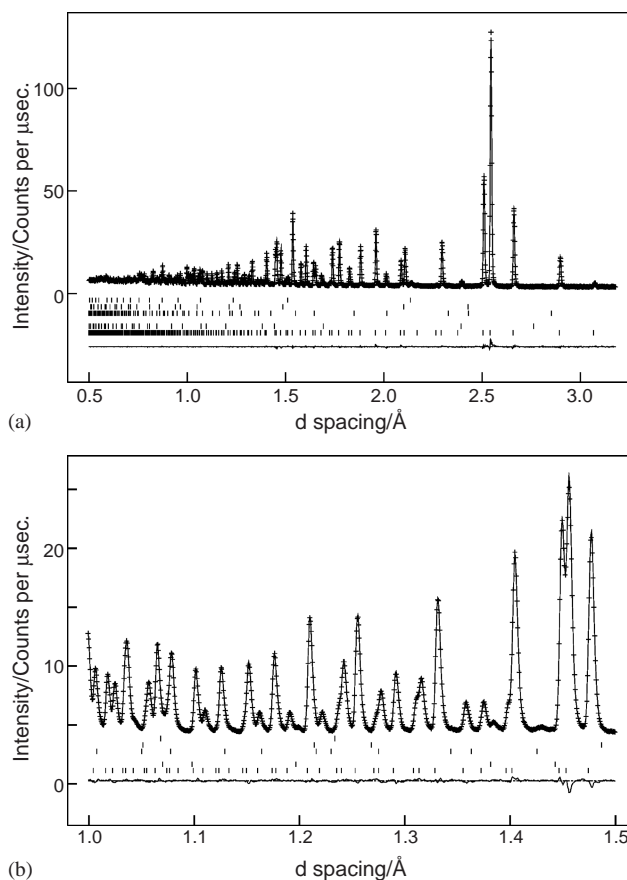The model used yielded also a very good fit with the synchrotron XRPD data (sample—$Ca_{1.87}Co_{0.87}Ga_{1.27}O_x$, $a = 15.01364(2)$ Å) recorded at room temperature

Fig. 1. Observed (crosses), calculated (solid line) and difference TOF NPD pattern for $Ca_7Co_3Ga_5O_{18}$, for (a) $d = 0.5$–3.8 Å and (b) for $d = 1$–1.5 Å. Reflection markers are from bottom up for $Ca_7Co_3Ga_5O_{18}$, CaO, Co_3O_4, CoO and V metal (sample container).

with $\lambda = 1.6071$ Å. The anomalous dispersion coefficients f' and f'' used for this data set were for Ca = 0.325, 1.383, for Co = −6.853, 3.932, for Ga = −1.235, 0.837, and for O = 0.050, 0.035. The residual indices were $\chi^2 = 2.62$, $wR_p = 9.3\%$, $R_p = 8.7\%$, $R_I = 2.9\%$, $R_F = 2.0\%$, $DwD = 0.80$, for 89 reflections in the 2θ range 9–90°. The fit between observed and calculated pattern is shown in Fig. 2b.

Atomic coordinates and atomic displacement parameters, both from TOF data and the synchrotron data recorded at 10 K, are given in Table 1. The agreement between them is good. There was no substantial difference between the structural parameters obtained from the two synchrotron data sets, recorded at, respectively, 10 K and room temperature, implying the absence of phase transition down to 10 K.

The SAED patterns of $Ca_7Co_3Ga_5O_{18}$ confirmed the face-centered unit cell found in Rietveld refinements, as seen in Fig. 3. There were no diffuse scattering or streaking in any of the ED patterns observed in the TEM study. The absence of extended structural defects was also confirmed in the HREM study (Fig. 4). The correctness of the structure model obtained from the
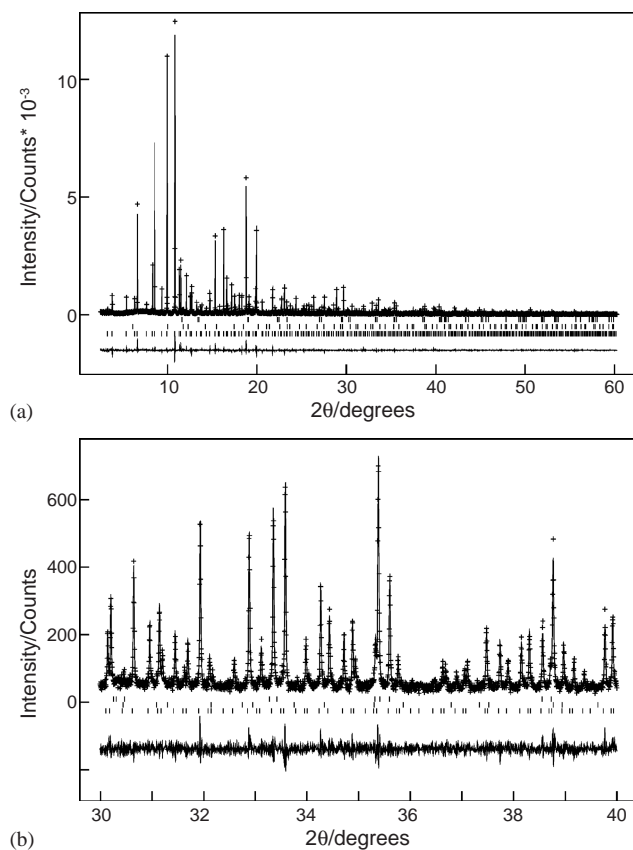
Fig. 2. Observed (crosses), calculated (solid line) and difference synchrotron XRPD pattern for $Ca_7Co_3Ga_5O_{18}$, recorded at 10 K, for (a) $2\theta = 2.5{-}60°$ and (b) $2\theta = 30{-}40°$. Reflection markers are from bottom up for $Ca_7Co_3Ga_5O_{18}$, Co_3O_4 and tetragonal CoO.
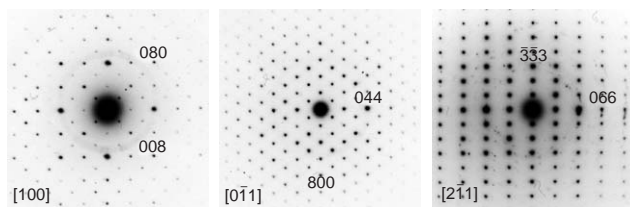
Fig. 3. SAED patterns of $Ca_7Co_3Ga_5O_{18}$, recorded along [100], [0$\bar{1}$1] and [2$\bar{1}$1].
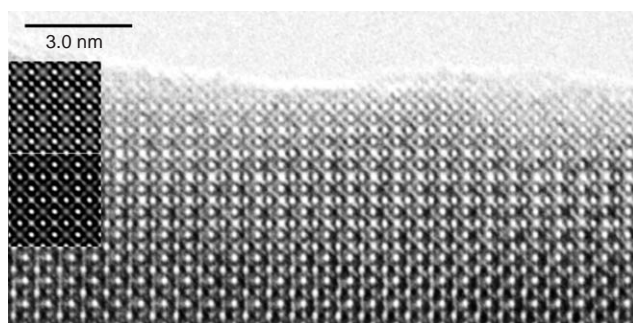
Fig. 4. HREM image of $Ca_7Co_3Ga_5O_{18}$, recorded along [100] and at a defocus value of –600 Å. The simulated HREM images were calculated at the corresponding defocus and thickness of 40 and 80 Å.

Rietveld refinements is also confirmed by the simulated HREM images, which show a good agreement with the observed ones.

3.2. Description of the structure

Selected atomic distances, corresponding to the coordinates refined from NPD data, are given in Table 2. In the $Ca_7Co_3Ga_5O_{18}$ structure (Fig. 5a), the Ca1 atoms are coordinated by 7 O atoms at 2.38–2.50 Å (only two of four O4 atomic positions are occupied simultaneously), and the Ca2 atoms by 6 O atoms at 2.32–2.37 Å, forming a distorted octahedron. A refinement of the neutron scattering length, or equivalently site occupancy factor (sof), of the octahedrally coordinated atom on the 4b site at (1/2,1/2,1/2) showed this site to be occupied by Co. The remaining 20 Co and 40 Ga atoms are then distributed over the tetrahedral sites $M1$–$M4$. No ordering of cobalt and gallium over these sites is here assumed and all four M sites are occupied by cobalt and gallium in a ratio Co:Ga = 1:2. The $M1$ atom is coordinated by a cube of O4 atoms. The sof for the O4 atom is however 1/2 and the coordination polyhedra around the $M1$ atom is therefore concluded to be a tetrahedron which is orientated at random in two ways. The $M2$ atom is coordinated by four O1 atoms at distance 1.8842(4) Å forming a tetrahedron. There are two partially occupied $M3$ and $M4$ tetrahedral sites in

Table 2
Atomic distances (Å) in $Ca_7Co_3Ga_5O_{18}$

Ca1–	O1 × 4	2.4964(4)	Ca2–	O1 × 3	2.3256(7)
	O3	2.3833(9)		O3 × 3	2.3685(5)
	O4 × 4	2.5950(6)			
Co–	O3 × 6	1.9631(6)	$M1$–	O4 × 8	1.818(1)
$M2$–	O1 × 4	1.8842(4)	$M3$–	O1 × 3	1.9391(6)
				O2	1.969(1)
				Mean	1.946
$M4$–	O1 × 3	1.8806(6)	$M3$–	$M4$	0.795(2)
	O4	1.935(3)			
	Mean	1.894			

Note: Atomic coordinates from NPD data.
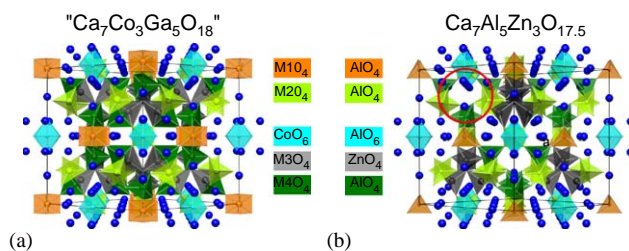
Fig. 5. Crystal structures of $Ca_7Co_3Ga_5O_{18}$ (a) and $Ca_7Al_5Zn_3O_{17.5}$ (b), viewed along [110]. The Ca atoms are shown as filled blue circles. One of the large voids in the crystal structure of $Ca_7Al_5Zn_3O_{17.5}$ is encircled.

the structure. The $M3$ and $M4$ tetrahedra share one face, implying that adjacent $M3$ and $M4$ sites cannot be simultaneously occupied (Fig. 5a). Refinement of the occupancies of these sites lead to the conclusion that they are not equally occupied (Table 1). The refined occupancy of the $M3$ site is 0.648(4) for the NPD data and 0.678(3) for the synchrotron data.

The four tetrahedral M sites form a disordered 3D-framework $(Co_{1/3}Ga_{2/3})O_2$ of corner-sharing M–O tetrahedra. There are large voids in the framework, around the $4b$ sites (1/2,1/2,1/2). These voids are filled with isolated CoO_6 octahedra and 8 surrounding Ca2 atoms. Each apex O atom of the octahedra is furthermore bonded to one Ca1 atom. This atom arrangement is illustrated in Fig. 6.

The $Ca_7Co_3Ga_5O_{18}$ structure can be compared with the structure of $Ca_7Al_5Zn_3O_{17.5}$. In the crystal structure of $Ca_7Al_5Zn_3O_{17.5}$ there are 2 different groups of the tetrahedra. In the first group (called cristobalite on Fig. 7a) all oxygen atoms are belonging to two tetrahedra. In the second group (called ZnS on Fig. 7a) four tetrahedra are connected to one oxygen atom. For the simplicity these two different groups of tetrahedra will be called CL1 and CL2 clusters, centered at (0,0,0) and (1/4, 1/4, 1/4), respectively. The same type of clusters can be found in the crystal structure of $Ca_7Co_3Ga_5O_{18}$. The arrangement of these clusters in the crystal structure of $Ca_7Co_3Ga_5O_{18}$ can be seen in Fig. 8. In the center of the first type of cluster, CL1, is the $M1$ tetrahedron, regularly orientated in the case of $Ca_7Al_5Zn_3O_{17.5}$ but randomly adopting two orientations in the case of $Ca_7Co_3Ga_5O_{18}$ (Figs. 7b and 8). The $M1$ tetrahedron shares its O4 atoms with the $M4$ tetrahedron and the cluster consists of the central $M1$ tetrahedron and the four surrounding $M4$ tetrahedra. There are 8 CL2 clusters consisting of 4 $M3$ tetrahedra that share a central O2 atom in the unit cell. In the ordered structure of $Ca_7Al_5Zn_3O_{17.5}$, there are four such

Fig. 7. Structural drawing showing a part of the crystal structure of $Ca_7Al_5Zn_3O_{17.5}$ (a) and how these can be combined in the average structure of $Ca_7Co_3Ga_5O_{18}$ (b). The partially occupied $M3$ and $M4$ tetrahedra are marked with arrows and the overlapping $M1$ tetrahedra are encircled.

Fig. 8. The two types of clusters in the $Ca_7Co_3Ga_5O_{18}$ structure. CL1 is centered at $4a$ (0,0,0) and CL2 at $8c$ (1/4,1/4,1/4).

CL2 clusters in the unit cell, with their centers at the $F23$ $4c$ sites (1/4,1/4,1/4), (3/4,3/4,1/4), (3/4,1/4,3/4) and (1/4,3/4,3/4), and the CL1 cluster at the unit cell origin is orientated so that face-sharing of tetrahedra belonging to the two types of clusters is avoided. This implies however that there are conspicuously large empty voids in the $Ca_7Al_5Zn_3O_{17.5}$ structure around the $F23$ $4d$ site (3/4,3/4,3/4), with a distance from the void centers to the nearest O atoms of 3.1 Å. This can be seen in Fig. 5b, where one these voids is encircled.

The main difference between the structures of $Ca_7Al_5Zn_3O_{17.5}$ and $Ca_7Co_3Ga_5O_{18}$ is that in the latter the $M3$ sites, belonging to CL2 type clusters, and the $M4$ sites, belonging to CL1 type clusters, are both fractionally occupied. In Fig. 7b, the partially occupied $M3$ and $M4$ tetrahedra are marked with arrows and the randomly oriented $M1$ tetrahedra are encircled. This implies that there are, in contrast to $Ca_7Al_5Zn_3O_{17.5}$, no, or very few, complete clusters in the $Ca_7Co_3Ga_5O_{18}$ structure, but only partial ones, with some of their tetrahedral sites empty. For $Ca_7Co_3Ga_5O_{18}$ there is a
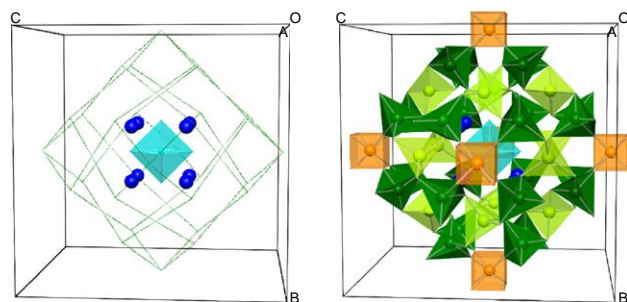

Fig. 6. Illustration of the large voids around the $4b$ sites (1/2,1/2,1/2) in the tetrahedral framework. The voids contain isolated Co^{3+}–O octahedra with 8 surrounding Ca2 atoms. Each O atom of the octahedra is furthermore bonded to one Ca1 atom. In the left-hand part, only the positions of the surrounding tetrahedral atoms are connected by lines, while the right-hand part shows the whole arrangement of the tetrahedra.
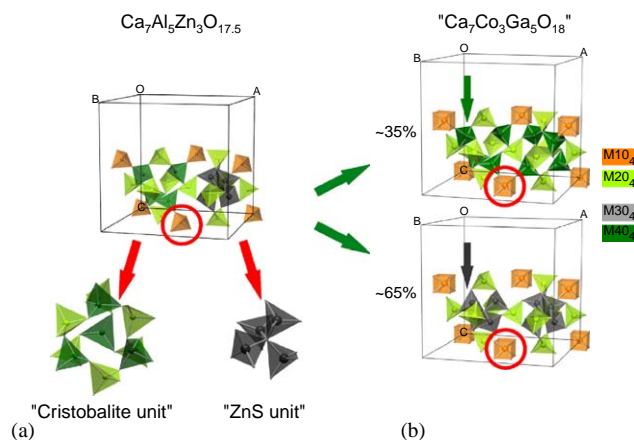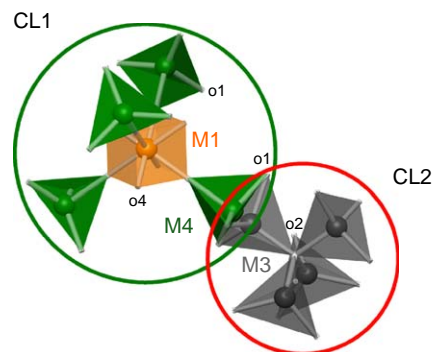
larger fraction of occupied tetrahedral sites that are part of (partial) CL2 type clusters, ca. 2/3, than for $Ca_7Al_5Zn_3O_{17.5}$, where only 1/2 of the corresponding positions are filled, in an ordered way. The central O2 atom position of the CL2 cluster is furthermore found to be fully occupied for $Ca_7Co_3Ga_5O_{18}$, whereas the corresponding position for $Ca_7Al_5Zn_3O_{17.5}$ is half empty, the empty positions being part of the large voids in the structure. This accounts for the larger oxygen content for $Ca_7Co_3Ga_5O_{18}$. If the vacant tetrahedral $M3$ sites for $Ca_7Co_3Ga_5O_{18}$ are truly distributed randomly, the average number of tetrahedra in the partial CL2 clusters is 2.67. For $Ca_7Co_3Ga_5O_{18}$ the fraction of occupied tetrahedral $M4$ sites per present CL1 cluster is, taking into account that the $M1$ tetrahedra are statistically oriented in two ways, ca. 2/3, corresponding to an average of 2.67 $M4$ tetrahedra linked to each $M1$ tetrahedron, in contrast to $Ca_7Al_5Zn_3O_{17.5}$, where all CL1 type clusters are complete.

3.3. Possible deviations from the ideal composition and metal atom distribution

The structure model described above has an ideal, statistical, Co/Ga atom distribution and several inherent assumptions: (i) the composition used is $Ca_7Co_3Ga_5O_{18}$, (ii) the $8c$ O2 site at the center of the CL2 cluster is assumed to be fully occupied, (iii) the four tetrahedral sites $M1$–$M4$ are all assumed to have equal fractions of Co and Ga atoms, (iv) the sum of the sof's for the $M3$ and $M4$ sites is assumed to be one. Although the fit for this model with observed intensities is very good, these assumptions will here in turn be addressed.

The compound formula used in the refinements, $Ca_7Co_3Ga_5O_{18}$, has a cation composition (47% Ca, 20% Co, 33% Ga) that differs slightly from the nominal composition, which was checked by chemical analysis, of the sample used for NPD (50% Ca, 20% Co, 30% Ga). This discrepancy cannot be accounted for by the observed impurity phases, whose amounts are too small to be significant here. The synchrotron XRD data were furthermore collected for a sample with another nominal composition (46% Ca, 22% Co, 32% Ga). The cation composition for this latter sample was checked by EDS micro-analysis, yielding 48.4(5)% Ca, 21.1(2)% Co, 30.4(6)% Ga. The unit cell parameters for these samples are, however, slightly different, 15.0558(3) and 15.0154(7) Å, respectively, indicating slightly different compositions. Further syntheses have confirmed that the phase indeed has a variable composition, with different Co:Ga ratios. We conclude that the ideal compound formula $Ca_7Co_3Ga_5O_{18}$ agrees within a few at% with the different nominal compositions, but that small differences in stoichiometry do occur for the phase. It was however not found possible to further improve the good fit with observed intensities in the

refinements by any changes from the $Ca_7Co_3Ga_5O_{18}$ stoichiometry.

The $M3$ tetrahedra in the CL2 cluster are found to be only approximately 2/3 filled, while the O2 atom site, at the center of the cluster, is assumed to be fully occupied in the refinement. It is, however, conceivable that the O2 site has a partial occupancy. This possibility is connected with the question whether the clusters are, as held likely, predominantly partial, i.e. one or more of its four $M3$ sites are empty, or if the clusters occur predominantly intact in the structure. In the former case, the O2 site would not be fully occupied and its sof could be as low as around 2/3. A refinement of the O2 sof yielded, however, a value of 0.933(6), with only insubstantial decreases in residual indices, which shows that the majority of CL2 clusters must be partial. One can propose that complete CL2 clusters can only be observed in the case when $M3$ tetrahedron is fully occupied by Co^{2+} atoms. The case of fully occupied CL2 clusters with Ga^{3+} contradicts to one of Pauling's rules [8]. According to this rule anion charge should be compensated by the strengths of the electrostatic valence bonds reaching to it from the cations at the centers of the polyhedra of which it forms a corner. Since the $M3$ site is predominantly occupied by Ga^{3+} the probability of the fully occupied CL2 clusters with Co^{2+} seems to be very low.

In the refinement, the four tetrahedral sites $M1$–$M4$ were all assumed to have equal fractions of Co and Ga atoms. Possible deviations from this ideal distribution could be examined by using the TOF NPD data set and independently refining the scattering lengths (or sof's) for the atoms on all four M sites. Calculated average scattering lengths for the ideal distribution, with a 1:2 ratio of Co and Ga atoms, are $M1 = 0.569$, $M2 = 0.569$, $M3 = 0.368(2)$, $M4 = 0.200(2) \times 10^{-12}$ cm, while the corresponding independently refined values were $M1 = 0.565(4)$, $M2 = 0.572(2)$, $M3 = 0.371(2)$ and $M4 = 0.184(2) \times 10^{-12}$ cm. The refined values show that the actual distribution is very close to the ideal one, with the only significant deviation found for the $M4$ site, amounting to ca. 8 e.s.d.'s. The corresponding fractions of Ga atoms on the $M1$ sites, 65.8(8)%, and $M2$ sites, 67.3(4)%, agree in particular very well with the ideal fraction of 2/3.

In the refinement, the assumption was furthermore made that the sum of the occupancies of $M3$ and $M4$ sites is equal to one. This assumption is largely supported by the independently refined scattering lengths for the M cations. Using here the ideal formula $Ca_7Co_3Ga_5O_{18}$ and a Co:Ga ratio of 1:2 on all M sites, the refined scattering lengths on the $M3$ and $M4$ sites correspond to a summed sof for these sites of $0.652(4) + 0.323(4) = 0.975(6)$.

Finally, if one adopts the last assumption, a sum of 1 for the sof's for the $M3$ and $M4$ sites, one can from

the refined scattering lengths calculate a structural formula per unit cell, $Ca_{56}Co_{24.9(2)}Ga_{39.1(2)}O_{144}$, which agrees reasonably well with the ideal one, $Ca_{56}Co_{24}Ga_{40}O_{144}$.

4. Discussion

The tentative composition used in the structure refinement is $Ca_7Co_3Ga_5O_{18}$, corresponding to a unit cell content of $Ca_{56}Co_{24}Ga_{40}O_{144}$. The average oxidation state of cobalt is accordingly $+2.33$ and a chemical formula per unit cell is $Ca_{56}Co_8^{3+}Co_{16}^{2+}Ga_{40}O_{144}$. There is no evidence in the diffraction data for any significant oxygen non-stoichiometry. Different synthesis yielded however phases with slightly varying unit cell parameters, between 15.01 and 15.05 Å, implying a variable composition. A probable solid solution substitution mechanism is $Co^{3+} \Leftrightarrow Ga^{3+}$.

Bond valences were calculated using the expression $bv = \exp((R_0 - R)/0.37)$ with the R_0 values Ca = 1.967, $Co^{2+} = 1.692$, $Co^{3+} = 1.68$ and Ga = 1.73 [9]. The bond valence sums (BVS) for Ca1 and Ca2 are 1.65 and 2.15, respectively. The Co–O distance in the octahedra is 1.9631(6) Å, yielding a BVS of 2.8 for Co^{3+}, and agrees with an expected distance of 1.95 Å, calculated from the Shannon–Prewitt ionic radii $r(Co^{3+},LS) = 0.545$ and $r(O) = 1.40$ [10]. For the tetrahedral sites $M1$–$M4$ the condition is complicated by the fact that they all have mixed occupancies and that the $M3$ and $M4$ sites are only partially occupied. BVS calculations for these sites are therefore not directly applicable. The $M1$ and $M2$ sites have as expected shorter M–O distances, 1.82 and 1.88 Å, respectively, than the average ones for the $M3$ and $M4$ sites, 1.95 and 1.89 Å, respectively, due to the partial occupancy of the latter. It is however not understood here then why the average $M3$–O distance is longer than the average $M4$–O distance. Expected tetrahedral and Co^{2+}–O and Ga–O distances are 1.98 and 1.87 Å, respectively. The M–O distances for the $M1$ and $M4$ sites are thus slightly shorter than expected and indicate that the remaining $4 Co^{3+}$ per unit cell occupies these sites. A calculation of the average oxidation state of the cobalt, using the above discussed assumptions concerning the oxidation states and the composition as determined from the NPD refinement, yields $+2.37$ which is in good agreement with the $+2.33$ obtained for the ideal composition $Ca_7Co_3Ga_5O_{18}$.

As mentioned above the TEM studies revealed no indications of streaking and superstructure reflections in selected area diffraction patterns, nor did the HREM images indicate an ordering of the statistically distributed Ga, Co and O atoms.

The study of the temperature dependence of the electrical conductivity and thermo-electric power of $Ca_7Co_3Ga_5O_{18}$ showed that the major charge carriers are electron holes (h^+), although the former was small and the latter rather large [3]. The large mobility activation energy 0.45 eV could be attributed to a large spatial separation of the cobalt ions in the structure. The hole concentration, was found to increase with increasing oxygen gas pressure pO_2. The present structure determination shows that all tetrahedral cobalt atom positions are also partially occupied by gallium atoms and that the Co–O octahedra are spatially separated. It thus provides an explanation for the low conductivity values and large activation energy for $Ca_7Co_3Ga_5O_{18}$.

5. Concluding remarks

The crystal structure of $Ca_7Co_3Ga_5O_{18}$ is a disordered variant of the structure of $Ca_7Al_5Zn_3O_{17.5}$. It can be described as a disordered three-dimensional framework of corner-sharing MO_4 tetrahedra, where M is 1/3 cobalt and 2/3 gallium. The framework contains two kinds of clusters. One type, CL1, has its center on the $4a$ site (0,0,0) and consists of a central $M1$ tetrahedron that is, via corner-sharing, connected to four surrounding $M4$ tetrahedra. The second type, CL2, has its center on the $8c$ site (1/4,1/4,1/4) and consists of 4 $M3$ tetrahedra that share the central O2 atom. In the voids of the tetrahedral framework CoO_6 octahedra and 8 surrounding Ca2 atoms are found. Varying unit cell parameters for different nominal starting compositions indicate a small solubility range, due to small variations in the Co/Ga content in the tetrahedra. The tetrahedral sites appear to be truly statistically occupied by Co and Ga atoms, as no indication of ordering was observed in the ED studies (streaking/superstructure) and the HREM images.

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