

Single-crystal X-ray diffraction study of CaIrO_3

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ABSTRACT

Single crystals of CaIrO_3 were prepared via flux growth method. Crystal structure parameters, including the anisotropic displacement parameters, are determined based on a single-crystal X-ray diffraction experiment. The unit-cell dimensions are $a = 3.147(2)$, $b = 9.866(6)$, and $c = 7.302(5)$ Å. The structure is a three-dimensional dense structure with small vacant spaces. The CaIrO_3 structure can be described as a pseudo-one-dimensional oxide and is compared with Ca_4IrO_6 structure. The IrO_6 octahedra are significantly distorted, in contrast to other octahedral Ir^{4+} compounds. The O-O distances for faces and edges shared between polyhedra are shorter than other non-shared edge distances. These effects are explained by Pauling's rules and occur to decrease the repulsion between the cations. Thermal vibrations of Ca and Ir atoms are significantly anisotropic. Thermal vibrations of Ca and Ir atoms are restricted in orientation toward the shared face, shared edges, and shortest cation-cation directions. The single-crystal experiment shows that CaIrO_3 crystals grow fastest along the *a* axis and that they assume a prism or needle shape. Strongly preferred orientation of such prism shaped CaIrO_3 -type post perovskite MgSiO_3 crystals may develop under the shear flow in the Earth's mantle.

Keywords: Post-perovskite, CaIrO_3 , single crystal, X-ray diffraction, lower mantle, D' layer

INTRODUCTION

The CaIrO_3 -type post-perovskite structure of MgSiO_3 has been shown experimentally and theoretically to occur at the temperature and pressure conditions of D'' layer of the lowest Earth's mantle, extending to 2700–2900 km depth (Murakami et al. 2004; Tsuchiya et al. 2004; Oganov and Ono 2004; Iitaka et al. 2004; Mao et al. 2004; Ono and Oganov 2005; Wentzcovitch et al. 2006; Shieh et al. 2006). The discovery of the post-perovskite phase has attracted considerable attention because of its potential relevance to the D'' layer. It has been inferred that the post-perovskite phase assumes platy crystal habit, with shortest direction parallel to the (010) plane, suggested from the sheet-stacking structure. Preferred orientation in this structure is an additional potential source of the anisotropy in D'' region (Murakami et al. 2004; Tsuchiya et al. 2004; Oganov and Ono 2004; Merkel et al. 2006; Wentzcovitch et al. 2006). Pressure-induced phase transitions leading to the CaIrO_3 -type structures have been reported in other familiar compounds, including MgGeO_3 , MnGeO_3 , Fe_2O_3 , Al_2O_3 , Mn_2O_3 , and NaMgF_3 (Hirose et al. 2005; Kubo et al. 2006; Tateno et al. 2006; Caracas and Cohen 2005; Oganov and Ono 2005; Tsuchiya et al. 2005; Ono and Ohishi 2005; Ono et al. 2006; Santillan et al. 2006; Liu et al. 2005; Martin et al. 2006a, 2006b). CaIrO_3 -type phases of these compounds are unquenchable to ambient conditions.

Phase relations and thermodynamic properties of compounds in the ternary systems Ca-X-O in air, where X is a metal from the platinum group, were investigated extensively because Pt-group metals are used for materials of melting pot and other high-temperature applications (McDaniel and Schneider 1972; Jacob et al. 1999). In the Ca-Ir-O system, three ternary compounds CaIrO_3 , Ca_2IrO_4 , and Ca_4IrO_6 have been identified at high temperature (McDaniel and Schneider 1972). The compound CaIrO_3 dissociates to Ir and Ca_2IrO_4 at 1408 K (McDaniel and Schneider 1972). The structure of CaIrO_3 was proposed by Rodi and Babel (1965), based on a single-crystal experiment, but the atomic coordinates reported in the paper are not correct. It is known that TlPbI_3 , FeUS_3 , AgTaS_3 , ThMnSe_3 , and UMnSe_3 (Noel and Padiou 1976; Wada et al. 1992; Kim et al. 1997; Ijjaali et al. 2004) have the same structure at ambient conditions.

The CaIrO_3 structure type is very important for understanding the structure and properties of the Earth's lowest mantle, therefore detailed knowledge of the structure is important not only for high-temperature and high-pressure crystal chemistry, but also for understanding the Earth's mantle. In this study, single crystals of CaIrO_3 were obtained by a flux method. The crystal-structure parameters, including the anisotropic displacement parameters, were determined based on a single-crystal X-ray diffraction experiment.

EXPERIMENTAL METHODS

Single crystals of CaIrO_3 were grown from a tenfold excess eutectic flux of CaCl_2 under atmospheric conditions. Reagent $\text{Ca}(\text{OH})_2$ and Ir were used. The

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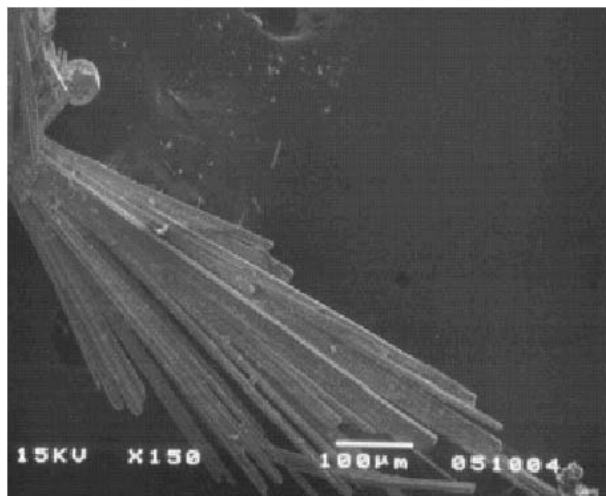


FIGURE 1. SEM images of the run products. Scale bars are 100 μm . The dimensions of the prismatic crystals are about $150 \times 15 \times 25 \mu\text{m}$.

starting materials were placed in a covered platinum crucible and heated in air at 1100 K for 8 h, and then cooled to 600 K at a rate of 10 K h^{-1} . The flux was dissolved in distilled water and dark needle crystals were collected for analysis. A SEM image of the crystals is shown in Figure 1. The X-ray powder diffraction pattern of obtained crystals was consistent with that reported for CaIrO_3 (McDaniel and Schneider 1972).

The unit-cell parameters and diffraction intensity data of the synthesized single crystal were measured at room temperature using a four-circle diffractometer (RIGAKU AFC5S) operated at 40 kV and 30 mA. Graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) was used for the measurements. The crystal size was $100 \times 10 \times 10 \mu\text{m}^3$. Results of space group determination indicated $Cmcm$ symmetry, which is consistent with previous studies (Noel and Padiou 1976; Tsuchiya et al. 2004). The unit-cell parameters were determined by least-squares refinement of 25 reflections. Lorentz and polarization corrections were applied, and absorption correction was made assuming that the sample is a cylinder, with a radius of 10 μm .

The crystal-structure refinements were carried out using a full matrix least-squares program RADY89 (Sasaki 1989). The structural parameters by Noel and Padiou (1976) were used as the initial values for the refinements. Anomalous dispersion coefficients and atomic scattering factors for ionic forms of Ca^{2+} , Ir^{4+} , and O^{2-} were taken from the *International Tables for X-ray Crystallography* (Ibers

and Hamilton 1974). After several cycles of refinement, isotropic displacement parameters were converted to the anisotropic model. The crystallographic data and data-collection and refinement parameters are listed in Tables 1 and 2. Selected interatomic distances are given in Table 3.

RESULTS AND DISCUSSION

Crystal structure and coordination environments

Figure 2 shows the crystal structure of CaIrO_3 . The structure has IrO_6 octahedra sharing edges to form rutile-type chains. These chains are interconnected by apical O atoms in the direction of the **c** axis to form edge and apex sharing octahedral sheets. The octahedral sheets are stacked along the **b** axis with interlayer Ca ions. On the other hand, the structure also consists of infinite one dimensional chains of CaO_8 polyhedra sharing the face of O2-O1-O2 (Fig. 3). These chains run along the **a** axis (Fig 3). These chains are interconnected by sharing O2-O2 edge in the direction of the **c** axis to form face and edge shared polyhedral sheets. The Ca polyhedral sheets are stacked along the **b** axis with interlayer Ir ions.

This structure has been described as a pseudo-two-dimensional layer structure (Murakami et al. 2004; Tsuchiya et al. 2004; Oganov and Ono 2004; Iitaka et al. 2004), whereas it is actually a three-dimensional dense structure with small vacant spaces, as discussed later. The CaIrO_3 structure can be also described as a pseudo-one-dimensional oxide because it has the chain of CaO_8 polyhedra along **a** axis, similar to Ca_4IrO_6 structure (Davis et al. 2001). Ca_4IrO_6 consist of one dimensional chains of face sharing trigonal prisms of CaO_8 and octahedral sheets of IrO_6 running parallel to the **c** axis. The chains in Ca_4IrO_6 are surrounded by CaO_8 distorted square antiprism. The CaIrO_3 structure consists of both the octahedral chain of Ir and the polyhedral chain of Ca running along the **a** axis (Figs. 2, 3a, and 3b). The Ca site is considered to be in eightfold coordination, and the CaO_8 polyhedron shares two face and 10 edges with surrounding CaO_8 polyhedra and IrO_6 octahedra. The CaO_8 polyhedron (a distorted hendecahedron) can be described as a trigonal prism with two additional oxide ions in the equatorial position (Fig. 4a) or a shape with a distorted square antiprism in which one of the squares is distorted in a O1-O2-O1-O2 lozenge (Fig. 4b). In Figure 4a, the bottom and cap triangle O2-O1-O2 faces of the trigonal prism are the shared faces in the CaO_8 polyhedral

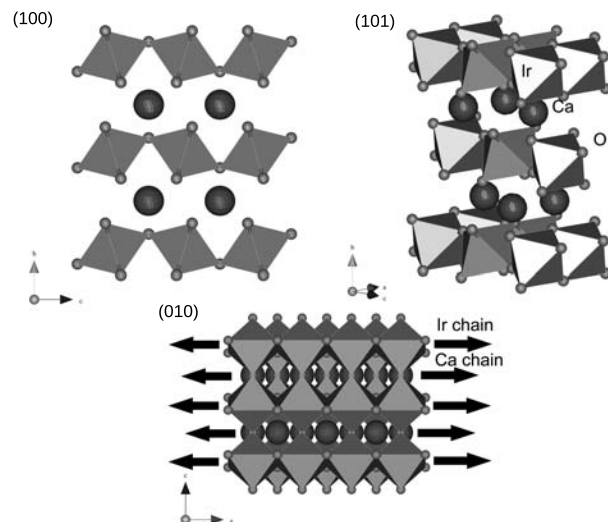


FIGURE 2. Crystal structure of CaIrO_3 .

TABLE 1. The crystallographic data and data-collection parameters

Sample size (μm^3)	$100 \times 10 \times 10$
<i>a</i> ($\text{\AA}$)	3.1472 (16)
<i>b</i> ($\text{\AA}$)	9.8655 (63)
<i>c</i> ($\text{\AA}$)	7.3018 (46)
<i>V</i> ($\text{\AA}^3$)	226.71 (23)
<i>Z</i>	4
Density (g/cm^3)	8.211
μ (cm^{-1})	64.09
Scan type	ω -2 θ
Scan speed ($^\circ/\text{min}$)	1
2 θ range	$8 < 2\theta < 120$
Range of <i>h k l</i>	$0 < h < 7, -20 < k < 20, -16 < l < 16$
<i>R</i> (%)	6.36
<i>wR</i> (%)	6.50
G.O.F.	2.72
Weighting scheme	$1/[\sigma(F_o)^2 + (R_{int} * F_o)^2]$
<i>R</i> _{int} (%)	7.43
Measured reflections	1085
Independent reflections with $ F_o > 3\sigma(F_o)$	377

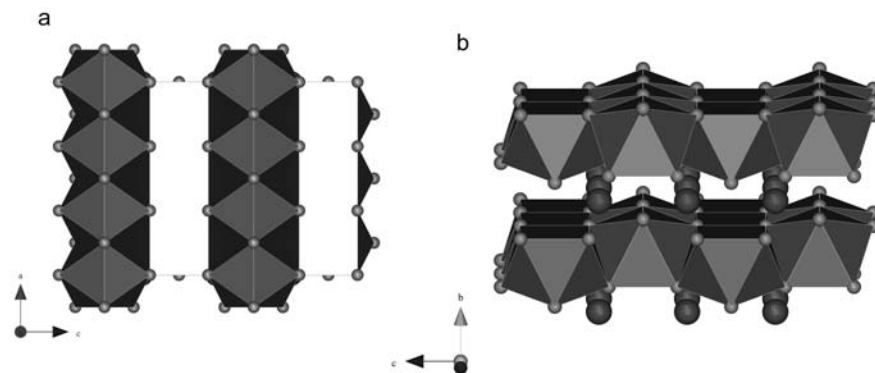


FIGURE 3. Perspective views of Ca polyhedral sheets (010) (a) and (100) (b).

TABLE 2. Refined positional parameters, equivalent isotropic displacement parameters, and anisotropic displacement parameters ($\times 10^4 \text{ \AA}^2$) for CaIrO_3

	x	y	z	B_{eq}
Ca	0	0.7492(6)	1/4	0.40(11)
Si	0	0	0	0.32(2)
O1	0	0.0779(28)	1/4	0.70(50)
O2	0	0.3658(19)	0.4452(28)	0.79(36)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	27(35)	80(3)	45(5)	0	0	0
Ir	26(6)	62.4(7)	33(1)	0	0	40(3)
O1	115(151)	42(12)	108(26)	0	0	0
O2	111(111)	76(9)	113(16)	0	0	-29(11)

TABLE 3. Atomic distances ($\text{\AA}$) and bond angles ($^\circ$) for CaIrO_3

Ca-O1 ($\times 2$)	2.31(2)	MnO ₈	
Ca-O2 ($\times 4$)	2.44(1)	O1-O1	3.1472(14)
Ca-O2 ($\times 2$)	2.51(2)	O1-O2 ($\times 4$)	2.76(2)*
		O1-O2 ($\times 4$)	3.23(3)†
Ca-Ca ($\times 2$)	3.1472(14)	O2-O2 ($\times 2$)	2.87(3)†
Ca-Ca ($\times 4$)	3.976(3)	O2-O2 ($\times 4$)	2.95(2)*
		O2-O2 ($\times 2$)	3.1472(14)*
Ir-O1 ($\times 2$)	1.978(8)	IrO ₆	
Ir-O2 ($\times 4$)	2.066(10)	O1-O2 ($\times 4$)	2.766(14)*
Ir-Ir ($\times 2$)	3.1472(14)	O1-O2 ($\times 4$)	2.95(2)
Ir-Ir ($\times 2$)	3.651(3)	O2-O2 ($\times 2$)	3.1472(14)*
		O2-O2 ($\times 2$)	2.68(2)*
O1-Ir-O2	86.3(2)		
O1-Ir-O2	93.7(2)		
Ir-O1-Ir	134.3		

* Shared edge.

† Shared plane.

chains and the coordination environments for cations are related to Ca_4IrO_6 structure (Davis et al. 2001).

The calculated interatomic distances and bond angles are listed in Table 3. The IrO_6 octahedra are distorted significantly, with Ir-O distances ranging from 1.98 to 2.10 $\text{\AA}$. There are two values of Ir-O distances in CaIrO_3 , although there is one value of Ir-O distances in Ca_4IrO_6 , $\text{Ca}_3\text{MgIrO}_6$, and $\text{Ca}_3\text{ZnIrO}_6$ (Davis et al. 2001). The O-Ir-O angles in IrO_6 octahedron also deviate largely from the ideal value of 90° .

The distance for the shared O2-O2 edge between IrO_6 octahedron is 0.38 $\text{\AA}$ shorter than other O2-O2 non-shared edge distance (Table 3). The O2-O2 distance, which is perpendicular to the *a* axis, is shortened to 2.77 $\text{\AA}$. This effect occurs to decrease the repulsion between Ir and Ir ions. The O-O distances for the edges of faces shared between the CaO_8 polyhedron and IrO_6 octahedron are also shorter than other distances. The O1-O2, O2-O2,

and O2-O2 distances are shortened to 2.78, 2.85, and 2.89 $\text{\AA}$, respectively. These effects can be explained by Pauling's rules (Pauling 1960), i.e., the O-O shared edge distance is shorter than other distances to decrease the repulsion among the cations.

THERMAL VIBRATION OF ATOMS

The displacement parameters, corresponding to the mean square displacement, can provide much useful information on thermal properties of minerals such as Debye-characteristic temperature, anharmonicity of thermal vibration, thermal expansion, effective potential, and diffusion path (Willis and Pryor 1975; Yoshiasa et al. 1987, 1997). The displacement parameter includes the effects of both static and dynamical disorder; the former is the configuration disorder, while the latter arises from thermal vibrations of atoms. The effect of both static and dynamical disorder is an intrinsic effect in the solid materials. All crystals have this type of disorder. The equivalent isotropic displacement parameters, B_{eq} (Table 2), for the Ca and Ir atoms are smaller than those for the O atoms. These values are comparable to displacement parameters found for related compounds, though those for the Mg atoms are the largest in MgSiO_3 perovskite structure (Sugahara et al. 2006), which is a related compound of post-perovskite.

The anisotropic displacement parameters, U_{ij} , in CaIrO_3 are given in Table 2. The amplitudes of U_{11} along the *a* axis are the smallest for the Ca and Ir atoms except for the O atom. The large amplitude of thermal displacements for Ca and Ir atoms are observed toward the *b* axis. The structure has a peculiar characteristic that the directional dependence of thermal properties is different for cation and anion.

Figures 5 and 6 show that the thermal ellipsoids calculated from anisotropic displacement parameters. Thermal vibrations of all atoms are significantly anisotropic, though uncertainties of U_{11} of Ca, O1, and O2 are large. Mean square displacements for Ca atoms are large in the direction parallel to the *b* axis.

Thermal vibrations of Ca and Ir atoms are restricted toward the shared face, shared edges and shortest cation-cation directions. Moreover, a component of thermal vibration toward the vacant space is added because the CaIrO_3 structure is a highly dense structure with small vacant spaces. A percentage of vacant spaces in CaIrO_3 is 37%, while that in MgSiO_3 perovskite is 38%. The largest amplitude of thermal vibration for Ca atom is directed toward vacant space in the IrO_6 octahedral chain (arrows in Fig. 5b). The largest amplitude for Ir atom is directed toward vacant space in the CaO_8 polyhedral chain (arrows in Fig.

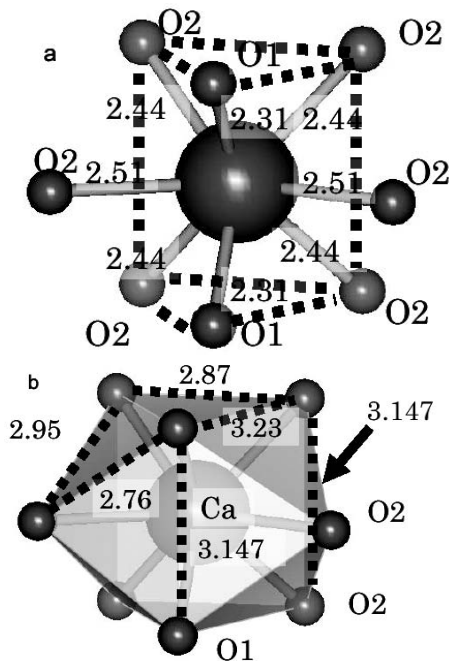


FIGURE 4. The coordination environment around Ca ion in CaIrO_3 . a and b are the Ca-O and O-O distances, respectively, in Å.

6b). The thermal vibrations of Ir atoms are also restricted in the direction perpendicular to the a axis and extended toward the second-nearest neighbor of Ca, the distance of which is 3.448 Å, while the distance of nearest-neighbor of Ca is 3.068 Å. The nearest Ca-Ca and Ir-Ir distances have the same value of 3.147 Å. The large anisotropy of thermal displacements of Ca and Ir atoms is observed approximately along the $[010]$ direction.

PSEUDO-ONE-DIMENSIONAL STRUCTURE AND CRYSTAL HABIT

In the region below the D'' discontinuity (Wyssession et al. 1989), strong seismic anomalies such as the seismic discontinuity, anisotropy (Lay et al. 1998) and anticorrelation between the observed shear and bulk sound velocities (Su and Dziewonski 1997) have been reported by recent seismic studies. It has been inferred that the layered structure of CaIrO_3 type post perovskite MgSiO_3 structure is potentially very anisotropic and preferred orientation in this structure is one of the origins of anisotropy in the D'' layer. The platy-shaped phase has large elastic anisotropy and develops preferred orientation in the shear flow that can result in strong seismic anisotropy below the D'' discontinuity (Merkel et al. 2006; Oganov and Ono 2004).

Many researchers studied the CaIrO_3 type post perovskite MgSiO_3 structure with a SiO_6 layered structure intercalated by eightfold-coordinated Mg ions (Murakami et al. 2004; Tsuchiya et al. 2004; Oganov and Ono 2004; Ono and Oganov 2005; Wentzcovitch et al. 2006; Iitaka et al. 2004). Although Oganov and Ono (2004) and Merkel et al. (2006) have proposed another possibility on preferred orientation of MgSiO_3 post-perovskite phase under shear from experiment and theory, it has also been proposed that silicate layers parallel to $\{010\}$ is probably the most natural slip plane oriented parallel to the convective flow (Oganov and Ono 2004). However, the structure is actually a

three-dimensional dense structure with small vacant spaces as discussed above. The single-crystal X-ray diffraction experiment shows that CaIrO_3 crystal grows toward the a axis, and it has a prism- or needle-shaped crystal habit (Fig. 1). Though it is possible that other methods of crystal growth or other crystallization conditions may lead to a different habit, prism- or needle-shape is the morphology exhibited when the CaIrO_3 crystal grows under conditions at room pressure and high temperature. This structure can be also described as a pseudo-one-dimensional structure. It was reported that the CaIrO_3 -type FeUS_3 and the related Ca_2IrO_6 type compounds do not form platy crystals, but prisms or rhombohedral-shaped crystals at high temperature (Noel and Padiou 1976; Davis et al. 2001). The Donnay-Harker's law and Periodic-Bond-Chain method were developed to describe the relation between the crystal habit and the structure (Donnay and Harker 1937; Hartman 1978; Yoshiasa 2001; Northrup and Reeder 1995). According to these rules, a crystal becomes needle-shaped when two axes in the unit cell are long and one axis is short. In contrast, a crystal develops a platy habit when one axis in the unit cell is long and two axes are short. In this latter case, only the space between the layers is open. Although the structure of CaIrO_3 is similar to a layer structure in the ac plane, crystal growth is not toward the c axis but only toward the a axis. Based on the crystal habit and the structural information, it is concluded that the CaIrO_3 structure cannot be considered exclusively as a layer structure because of its prismatic or needle-shaped habit.

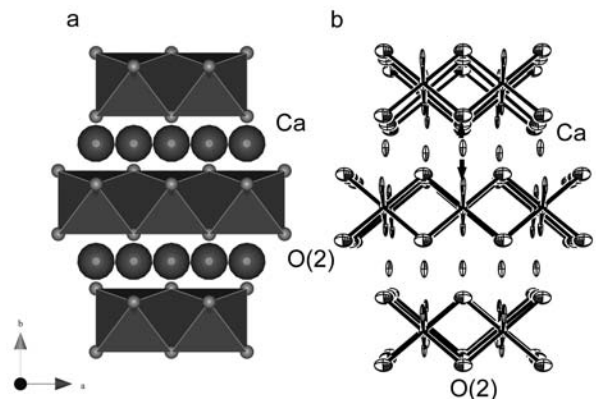


FIGURE 5. The crystal structure of CaIrO_3 in the (001) view. Polyhedra (a) and displacement ellipsoids (99% probability) (b).

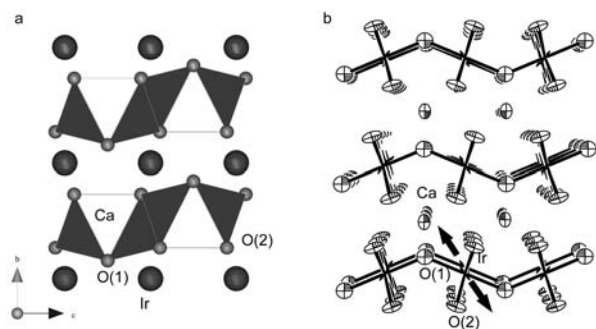


FIGURE 6. The crystal structure of CaIrO_3 in the (100) view. Polyhedra (a) and displacement ellipsoids (99% probability) (b).

It is plausible that in postperovskite the primary slip system involves (010). Lateral material displacement should then align mainly silicate layers parallel to the horizontal plane (010). However, this simple picture does not provide a satisfactory explanation for anisotropy in D'' and static elastic calculations have shown that $(V_{\text{sh}} - V_{\text{sv}})$ in transversely isotropic aggregates with this preferred orientation of platy crystals is small (Wentz-covitch et al. 2006; Stackhouse et al. 2005). It may be able possible to explain this disagreement assuming a needle- or prismatic-shaped crystal habit elongated parallel to the [100] direction, and not a layer structure. Strong preferred orientation of such prismatic-shaped CaIrO_3 type post perovskite MgSiO_3 crystals may develop under the shear flow.

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