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Matthieu Kauffmann, Nathalie Tancret, Francis Abraham, Pascal Roussel. New cobaltite materials containing CdI₂-type layers: Synthesis and structures of Ba₂Co₄ClO₇ and Ba₂Co₄BrO₇. *Solid State Sciences*, 2007, 9, pp.885-894. 10.1016/j.solidstatesciences.2007.06.012 . hal-00187411

HAL Id: hal-00187411

<https://hal.science/hal-00187411v1>

Submitted on 15 Nov 2007

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New cobaltite materials containing CdI₂-type layers: synthesis and structures of Ba₂Co₄ClO₇ and Ba₂Co₄BrO₇

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Abstract

Single crystals of the title compounds were prepared by solid-solid reaction using BaCl₂ or BaBr₂ flux at 1100°C. The structures of these two new cobaltites were solved and refined in the trigonal symmetry with space group $R\bar{3}m$: $a=5.716(2)$ Å, $c=45.01(3)$ Å for Ba₂Co₄ClO₇ and $a=5.7434(5)$ Å, $c=46.151(9)$ Å for Ba₂Co₄BrO₇. The two compounds are isostructural and their structures can be considered as the intergrowth along [001] of hexagonal blocks (Ba₂Co₈O₁₄)²⁻ built from a close-packing of [O₄] and [BaO₃] layers with octahedral and tetrahedral cobalt, separated by fluorite-type double layers (Ba₂Cl₂)²⁺ or (Ba₂Br₂)²⁺. The main difference between Ba₂Co₄ClO₇ and Ba₂Co₄BrO₇ is due to the fluorite-type layers: (Ba₂Cl₂)²⁺ double layers are perfectly ordered while (Ba₂Br₂)²⁺ blocks are affected by a structural disorder through the bromine atoms.

Keywords: Cobaltites, Barium cobalt oxyhalide, Hexagonal perovskite, Maximum Entropy Method (MEM), Crystal structure

1. Introduction

Numerous perovskite-related materials exhibit unusual and interesting properties such as high T_c superconductivity, piezo-electricity or colossal magneto-resistance among others [1, 2]. These phenomena are still insufficiently understood and the comprehension of the mechanism leading to these spectacular properties is of particular interest for the scientists working in the area of new materials. Therefore perovskite-type compounds are intensively studied. In this way, for instance, the well-known manganites have been largely investigated because of their interesting properties: a wide range of valence states and the possibility to adopt several polyhedral configurations as, for example, octahedral or tetrahedral environments. The research on manganites materials has led, for example, to the discovery of colossal magneto-resistance [3, 4]. Compared to these compounds, the cobaltites exhibit one additional degree of freedom provided by the cobalt spin-state. Indeed, Co^{3+} atoms ($3d^6$) in O_6 octahedral environment can adopt either the low spin LS ($t_{2g}^6 e_g^0$, $S=0$), the intermediate spin IS ($t_{2g}^5 e_g^1$, $S=1$) or the high spin HS ($t_{2g}^4 e_g^2$, $S=2$) configurations [5, 6]. The possibility to stabilize several spin configurations is of great interest, as illustrated for instance in the $\text{LnBaCo}_2\text{O}_{5.5}$ series where the metal-insulator transition is due to a spin-blockade mechanism attributed to the presence of high-spin and low-spin of Co^{3+} ions [7]. Moreover, the discovery of large thermopower properties in Na_xCoO_2 [8] has reinforced the interest of the research in cobaltites materials. In this series of layered cobalt oxides, candidates for thermoelectric materials, CdI_2 -type layers were proposed to be at the origin of these interesting physical properties.

Recently, Sun *et al.* have reported the existence of a new barium cobaltite series $\text{Ba}_{n+1}\text{Co}_n\text{O}_{3n+3}(\text{Co}_8\text{O}_8)$, in which $\text{Ba}_2\text{Co}_9\text{O}_{14}$ and $\text{Ba}_3\text{Co}_{10}\text{O}_{17}$ ($n=1$ and $n=2$ terms, respectively) were isolated [9]. These structures have been described as intergrowth of

perovskite layers and CdI₂-type oxide layers. These CoO₂ layers (of CdI₂-type) are also present in the misfit layered cobaltites series [Tl_{1-x}Sr_{2+x-y}Co_yO₃][CoO₂]_z and seem to be responsible of the very interesting high thermopower or low resistivity properties of these materials [10].

In the present paper, we report on the synthesis and structural characterization of two new isostructural oxyhalide cobaltites, Ba₂Co₄ClO₇ and Ba₂Co₄BrO₇, which adopt hexagonal 18R structures (18R meaning that 18 layers are necessary to describe the unit cell in space group R $\bar{3}$ m). These structures can be described by the stacking along [001] of fluorite-type double layers (Ba₂Cl₂)²⁺ or (Ba₂Br₂)²⁺ and blocks (Ba₂Co₈O₁₄)²⁻ built up from CdI₂-type oxide layers, which make them potential candidates for thermoelectric materials.

2. Experimental

2.1 Synthesis

Ba₂Co₄ClO₇ and Ba₂Co₄BrO₇ single crystals were grown using a flux technique. A 1:1:10 molar mixture of BaCO₃, Co₃O₄ and BaCl₂·2H₂O or BaBr₂·2H₂O was well ground in an agate mortar and heated in air at 1100°C for 48 hours in an alumina crucible. The mixture was then slowly cooled at 30°C/h to room temperature. After dissolving the excess of BaCl₂ or BaBr₂ with hot water, black hexagonal plate-like crystals of approximate size 0.1 - 2 mm were isolated from the reaction product.

Well-developed single crystals were analyzed by energy-dispersive X-ray spectroscopy on a JEOL JSM-5300 scanning microscope equipped with an IMIX system of Princeton Gamma Technology. Measurements revealed the presence of barium, cobalt, oxygen and chlorine or bromine for Ba₂Co₄ClO₇ and Ba₂Co₄BrO₇ respectively. Semi-

quantitative analysis realized on several points of the crystals confirmed the formula of each compounds.

2.2 Crystal structure determination

For the structure determination, single crystals of $\text{Ba}_2\text{Co}_4\text{ClO}_7$ and $\text{Ba}_2\text{Co}_4\text{BrO}_7$ were selected, mounted on a glass fibre and aligned on a Bruker X8 APEX2 diffractometer. Intensities were collected at room temperature using $\text{MoK}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) selected by a graphite monochromator. The ω -scan angle and the D_x parameter (distance between the single crystal and the CCD detector) were fixed, respectively, to $0.3^\circ/\text{frame}$ and 54 mm for $\text{Ba}_2\text{Co}_4\text{ClO}_7$ and to $0.5^\circ/\text{frame}$ and 40 mm for $\text{Ba}_2\text{Co}_4\text{BrO}_7$, depending on the crystal quality and spot shapes. For both compounds, acquisition time was 20 seconds per frame. The diffracted intensities were collected up to $2\theta=62.46^\circ$ with 2763 reflections and a redundancy of 4.86 in the space group $R\bar{3}m$ for $\text{Ba}_2\text{Co}_4\text{ClO}_7$ and $2\theta=56.88^\circ$ with 3512 reflections and a redundancy of 7.47 in the space group $R\bar{3}m$ for $\text{Ba}_2\text{Co}_4\text{BrO}_7$. After data collection, the intensities were integrated and corrected for Lorentz, polarisation and background effects using the Saint 7.12 software [11]. The SADABS 2006/1 program [12] was used to correct absorption effects using a semi-empirical method based on redundancy. Details of the data collection and refinements are given in Table 1. The hexagonal unit-cell parameters were refined to $a=5.716(2) \text{ \AA}$, $c=45.01(3) \text{ \AA}$ and $a=5.7434(5) \text{ \AA}$, $c=46.151(9) \text{ \AA}$ for $\text{Ba}_2\text{Co}_4\text{ClO}_7$ and $\text{Ba}_2\text{Co}_4\text{BrO}_7$ respectively.

Crystal structures were determined for both compounds in the $R\bar{3}m$ space group by direct methods using SIR97 program [13], which readily established the heavy atom positions (Ba, Co and Cl or Br). Oxygen atoms positions were found by difference Fourier map calculations. Anisotropic displacement parameters were attributed to all atoms in the last

cycles of refinement. Full-matrix least-squares structures refinements against F were carried out using the JANA2000 program [14].

As already reported in one of our previous paper [15], the introduction of bromine atoms in this type of layered compounds can lead to structural disorder. We thus undertook a Maximum Entropy Method (MEM) analysis of the diffraction data collected on Ba₂Co₄ClO₇ and Ba₂Co₄BrO₇. MEM is a model-free method which is used to calculate accurate electron densities in solids using experimental phased structure factors as input. This method has been proved to be particularly suited to determine structural aspects of disorder and anharmonic vibrations [16]. To calculate the precise electron density distribution, the MEM analysis was carried out using the computer program BAYMEM [17]. The total number of electrons in the unit cell has been fixed to F(000) values (1758 e⁻ and 1866 e⁻ for Ba₂Co₄ClO₇ and Ba₂Co₄BrO₇ respectively) and the unit cell was divided in a grid of 72*72*486 pixels to ensure a good resolution (better than 0.1 Å for the two studied compounds). All calculations were performed with an initial flat electron density with all the independent reflections. The

reliability factor of the MEM, $R_{MEM} = \frac{\sum |F_{obs} - F_{MEM}|}{\sum |F_{obs}|}$ is given in Table 1 (F_{obs} is obtained by the structural refinement and F_{MEM} is the structure factor calculated from the electron density obtained by the MEM).

3. Results and discussion

The atomic coordinates and anisotropic displacement parameters deduced from the single crystal refinements are listed in Table 2 and Table 3 for Ba₂Co₄ClO₇ and Ba₂Co₄BrO₇, respectively. Selected bond lengths and bond valence sums (BVS) are reported in Table 4 and Table 5. Views of the structures along (010) are represented Figure 1a and 1b. The two

compounds are isostructural and can be described as perovskite-related materials with a 18-layers stacking along the c-axis of [O₄], [BaO₃] and [BaX] (X=Cl or Br) layers. In the stacking sequence, two [O₄] layers are sandwiched by two [BaO₃] layers, leading to the creation of octahedral and tetrahedral sites where the cobalt atoms are localized. These blocks are separated by double fluorite-type (Ba₂X₂)²⁺ layers. Thus, the structure can be considered as the intergrowth of two different types of blocks represented by a (cccch'h')₃ stacking sequence with the notation of Katz and Ward [18] (where h' denotes a lacunar [BaX] layer): one hexagonal close-packed block (Ba₂Co₈O₁₄)²⁻ and one fluorite-type double layers (Ba₂Cl₂)²⁺ or (Ba₂Br₂)²⁺.

(Ba₂Co₈O₁₄)²⁻ blocks have recently been evidenced in Ba₂Co₉O₁₄ and Ba₃Co₁₀O₁₇ [9, 19]. These compounds have been described as intergrowth structures containing CdI₂-type layers (formed from two close-packed oxygen layers) and perovskite-type layers (built from [BaO₃] layers) with either a single-octahedral layer (Ba₂Co₉O₁₄) or a double-octahedral layer (Ba₃Co₁₀O₁₇). The CdI₂-type and the perovskite-type layers are connected together through a so-called "interface layer" containing octahedral and tetrahedral sites. Figure 2 presents the similarities between the structures of Ba₂Co₄XO₇ (X=Cl or Br) and those obtained for Ba₂Co₉O₁₄ and Ba₃Co₁₀O₁₇ viewed along [010]. It is thus possible to make an analogy with the compounds described by *Sun et al.*: in the oxyhalides, the (Ba₂Co₈O₁₄)²⁻ blocks are composed by a CdI₂-type block and the "interface layer" of the Ba₂Co₉O₁₄ and Ba₃Co₁₀O₁₇ compounds. The main difference between these two classes of materials lies in the connection between the blocks: while in Ba₂Co₉O₁₄ and Ba₃Co₁₀O₁₇, the (Ba₂Co₈O₁₄)²⁻ blocks are linked together by one or two octahedra respectively (in white on Figure 2), in Ba₂Co₄XO₇ they are clearly disconnected the ones from the others by double (Ba₂Cl₂)²⁺ or (Ba₂Br₂)²⁺ layers. One could thus imagine the formation of Ba₂Co₉O₁₄ by removing the (Ba₂Cl₂)²⁺ or (Ba₂Br₂)²⁺

layers of $\text{Ba}_2\text{Co}_4\text{XO}_7$ ($\text{X}=\text{Cl}$ or Br) and connecting the "interface layers" *via* an octahedral CoO_6 slice. Such types of relations between oxides and oxyhalides have been recently reported in oxychlorides and oxybromides of ruthenium with hexagonal perovskite-type structures [15, 20].

Another way to describe the oxyhalides under study is to refer to the well known series of spinel oxides [21]. Indeed, spinel can be described as the alternate stacking of different types of polyhedral layers: a cation deficient octahedral layer (whose cationic lattice is called *Kagomé*, see hereafter) and a mixed layer built up from corner-sharing octahedra and tetrahedra. The $(\text{Ba}_2\text{Co}_8\text{O}_{14})^{2-}$ blocks can thus be described using the formalism developed for the spinel oxides:

- The central block is formed by the (AB) stacking of $[\text{O}_4]$ layers, thus creating a sheet of edge-sharing cobalt-octahedra (Figure 3a). This arrangement can be considered as a *Kagomé* lattice (Figure 3b), denoted in the literature (Oc_3), in which all octahedral sites are fully occupied. Co(1) atoms are in the real octahedral sites of the *Kagomé* lattice whereas Co(2) occupy the *Kagomé* windows. This distribution leads to a complete octahedral layer of the CdI_2 -type but with two different crystallographic sites for the cobalt atoms. By analogy to the (Oc_3) layer, we will note this fully occupied *Kagomé* lattice (Oc_4). Numerous compounds are constituted of (Oc_3) octahedral layers, like for example, the spinel oxide MgAl_2O_4 [22], the olivine $(\text{Mg,Fe})_2\text{SiO}_4$ [23] or the double hexagonal LiFeSnO_4 [24]. In the present compounds, the calculated valence bond sums for Co(1) and Co(2) indicate a $\text{Co}(1)^{3+}/\text{Co}(2)^{2+}$ distribution. Furthermore, the average Co-O bond lengths of 1.915(7) Å for Co(1) and 2.078(7) Å for Co(2) in $\text{Ba}_2\text{Co}_4\text{ClO}_7$ (1.927(9) Å for Co(1) and 2.100(8) Å for Co(2) in $\text{Ba}_2\text{Co}_4\text{BrO}_7$) confirm the $\text{Co}(1)^{3+}/\text{Co}(2)^{2+}$ repartition with bond distances longer for Co^{2+} than for Co^{3+} , in agreement with the charge distribution proposed in $\text{Ba}_2\text{Co}_9\text{O}_{14}$ [9].

- The second type of sheet is built up from corner-sharing octahedra and tetrahedra, resulting from the (AB) stacking of [O₄] and [BaO₃] layers (Figure 4a). Each tetrahedron is connected to three octahedra through the oxygen of the [BaO₃] layer. This *mixed-polyhedra* block can be considered as a (Te₂Oc) layer (Figure 4b) in which one half of tetrahedral sites are empty. This kind of (TeOc) layer has been already evidenced in the LiLnMo₃O₈ compound for example [25]. The bond valence sums calculation for octahedral Co(3) suggest a Co³⁺ valence state. The Co-O bond distance of 1.946(8) Å for both Ba₂Co₄ClO₇ and Ba₂Co₄BrO₇ materials is similar to the Co(1)³⁺-O bond length of the *Kagomé* layer, confirming the suggested Co(3)³⁺ valence state. Finally, the BVS calculation for Co(4) indicates a slightly over-bonded character. However, as commonly observed in this kind of materials, one should note the possibility of oxygen vacancies, thus leading to a possible Co(4)²⁺ tetrahedral cobalt.

In the literature, two kinds of junction have been observed to connect an (Oc₃) block with a (Te₂Oc) layer:

- the junction J_{K/T} is obtained by the occlusion of the *Kagomé* windows by a tetrahedron of the (Te₂Oc) layer (Figure 5a). In this configuration, the tetrahedron shares three corners with the octahedra of the *Kagomé* windows. This kind of J_{K/T} junction is observed, for example, in the spinel oxide structure [22].

- the junction J_{K/O} exists when a *Kagomé* windows is blocked by an octahedron of the (Te₂Oc) layer by sharing three corners (Figure 5b). This type of J_{K/O} junction has been evidenced for double hexagonal LiFeSnO₄ [24].

In the same manner, J_{K/T} and J_{K/O} junctions have been reported for connecting (Oc₃) and (TeOc) layers (Figure 5c and 5d). For example, in LiLnMo₃O₈ [25], the (Oc₃) and (TeOc) layers are connected alternatively by J_{K/T} and J_{K/O} junctions.

In the compounds reported here, the junction between (Oc₄) and (TeOc) layers is ensured by sharing the corners of polyhedra, the oxygen atoms of [O₄] layers making the connexion between the two blocks. Central O(1) oxygen of tetrahedral Co(4) units is the common oxygen of three edge-sharing Co(1) octahedra while O(2) oxygen of octahedral Co(3) units ensures the connexion between three Co(2) octahedra. To our knowledge, it is the first time that this kind of junction is observed for the connection of (Oc₃)-like (= (Oc₄)) and (TeOc) layers. In that way, the connections of polyhedral layers in Ba₂Co₄ClO₇ and Ba₂Co₄BrO₇, as compared to the different types of junctions previously reported in the literature, can be considered as a J_{K/O} junction translated by $(a+b)/2$ (Figure 6a), hereafter noted J_{K/O}^{*}. In summary, the (Ba₂Co₈O₁₄)²⁻ block viewed along [010] (Figure 6b) can be schematized as a (TeOc)-(Oc₄)-(TeOc) stacking, with a J_{K/O}^{*} junction between each layer.

The (Ba₂Cl₂)²⁺ double layers are completely related to the reference structure *fluorite* (CaF₂) [26]. This later consists of infinite planes of Ca and F, thus making a compact framework of FCa₄ tetrahedra. On Figure 7 is presented the (Ba₂Cl₂)²⁺ block of Ba₂Co₄ClO₇ viewed along [010] (a) and the fluorite structure viewed along [011] (b). One should note the perfect similitudes between the (Ba₂Cl₂)²⁺ double layers and an isolated (Ca₂F₂)²⁺ block of fluorite. In this way, we can consider the (Ba₂Cl₂)²⁺ blocks in Ba₂Co₄ClO₇ as fluorite-type double layers.

The (Ba₂Br₂)²⁺ double layers of Ba₂Co₄BrO₇ are strongly related to the (Ba₂Cl₂)²⁺ blocks but with some interesting differences. While Ba(1) atoms occupy exactly the same position (6c), the positions of halides are modified, considering Cl or Br atoms. The most significant two- and three-dimensional electron density (ED) images in the region of the

chlorine and bromine atoms are shown in Figure 8. These images clearly shows that while the chlorine atom Cl(1) is localised on its $6c$ site (a), bromine is split over two distinct positions: Br(1) displays a triangular shape around a $6c$ site (b), occupying a $18h$ site at 25%, and Br(2) is split on a $6c$ position occupied at 25 % (c). Note that the occupations have been constrained together to fulfill the chemical composition $\text{Ba}_2\text{Co}_4\text{BrO}_7$. In summary, atoms in the area of the $(\text{Ba}_2\text{Br}_2)^{2+}$ double layers are affected by a structural disorder, while the other atoms are well ordered. This aspect has already been pointed out for other compounds containing bromine atoms [15].

4. Conclusion

To summarize the main findings of the work presented here, we have determined the structures of two new isostructural cobaltites. They are built by the stacking of fluorite-type layers and interesting blocks containing (CoO_2) layers. The role of the halide seems to be of particular interest for the modification of the structures: replacing the chlorine by a bromine atoms leads to the creation of disordered layers. This last point confirms the previously studies made on barium ruthenates with either chlorine- or bromine-based layers [15, 20]. Syntheses of pure powders suitable for a full physical characterization are in progress.

Supporting Information Available:

Further details concerning the nuclear structures determinations and the Maximum Entropy Method analysis may be obtained upon request from the authors.

Acknowledgements:

M. K. is indebted to “CNRS” and “Région Nord Pas-de-Calais” for financial support. The “Fonds Européen de Développement Régional (FEDER)”, “CNRS”, “Région Nord Pas-de-Calais” and « Ministère de l’Education Nationale, de l’Enseignement Supérieur et de la Recherche” are acknowledged for fundings of X-ray diffractometers. The authors want to thank Dr Olivier Mentré for fruitful discussion.

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Figure Caption

Figure 1: View along [010] of (a) $\text{Ba}_2\text{Co}_4\text{ClO}_7$ and (b) $\text{Ba}_2\text{Co}_4\text{BrO}_7$

Figure 2: View along [010] of (a) $\text{Ba}_2\text{Co}_4\text{XO}_7$, (b) $\text{Ba}_2\text{Co}_9\text{O}_{14}$ and (c) $\text{Ba}_3\text{Co}_{10}\text{O}_{17}$. The $(\text{Ba}_2\text{Co}_8\text{O}_{14})^{2-}$ blocks encountered in the two series are encircled with dotted lines.

Figure 3: Schematic representations of (a) central block of edge-sharing octahedra (Oc_4) of $\text{Ba}_2\text{Co}_4\text{ClO}_7$ and $\text{Ba}_2\text{Co}_4\text{BrO}_7$ and (b) true Kagomé lattice (Oc_3) with its windows

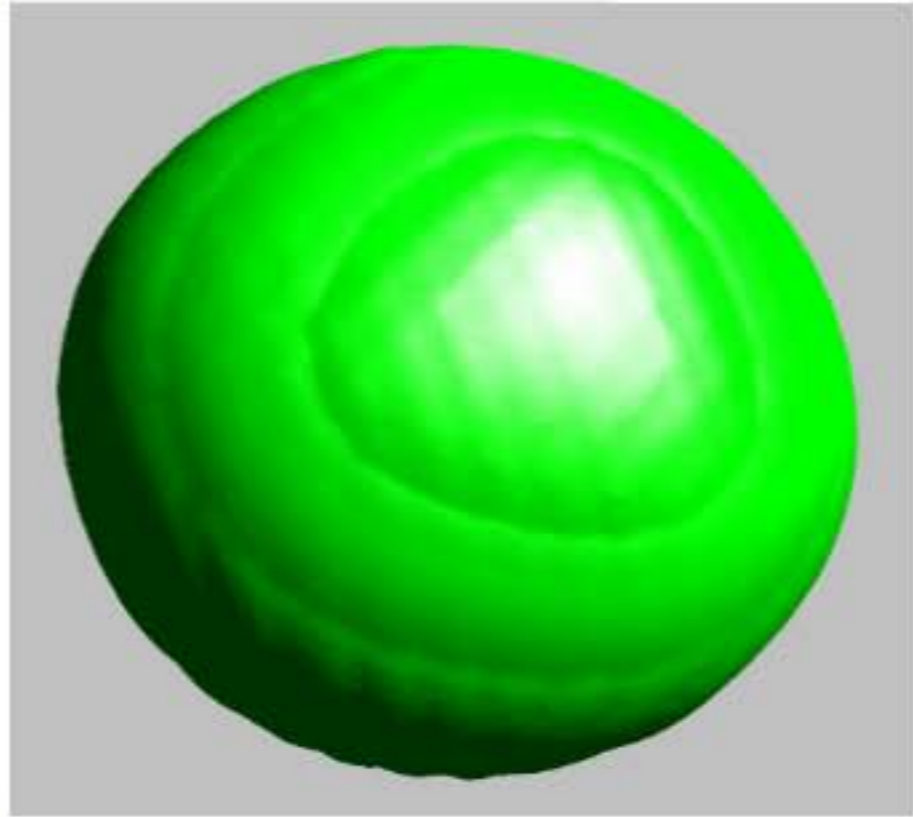
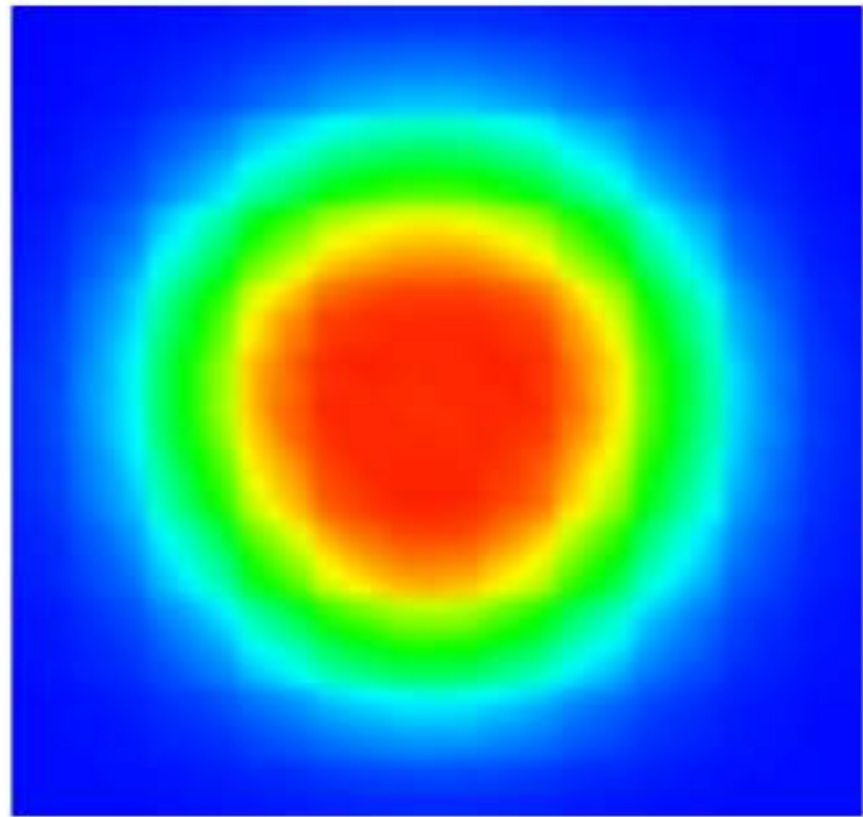
Figure 4: Schematic representations of mixed layers built up from corner-sharing octahedra and tetrahedra (a) (TeOc) layer of $\text{Ba}_2\text{Co}_4\text{ClO}_7$ and $\text{Ba}_2\text{Co}_4\text{BrO}_7$ and (b) (Te_2Oc) layer

Figure 5: Schematic representations of the different types of junctions: (a) $\text{J}_{\text{K/T}}$ between (Oc_3) and (Te_2Oc) – (b) $\text{J}_{\text{K/O}}$ between (Oc_3) and (Te_2Oc) – (c) $\text{J}_{\text{K/T}}$ between (Oc_3) and (TeOc) – (d) $\text{J}_{\text{K/O}}$ between (Oc_3) and (TeOc)

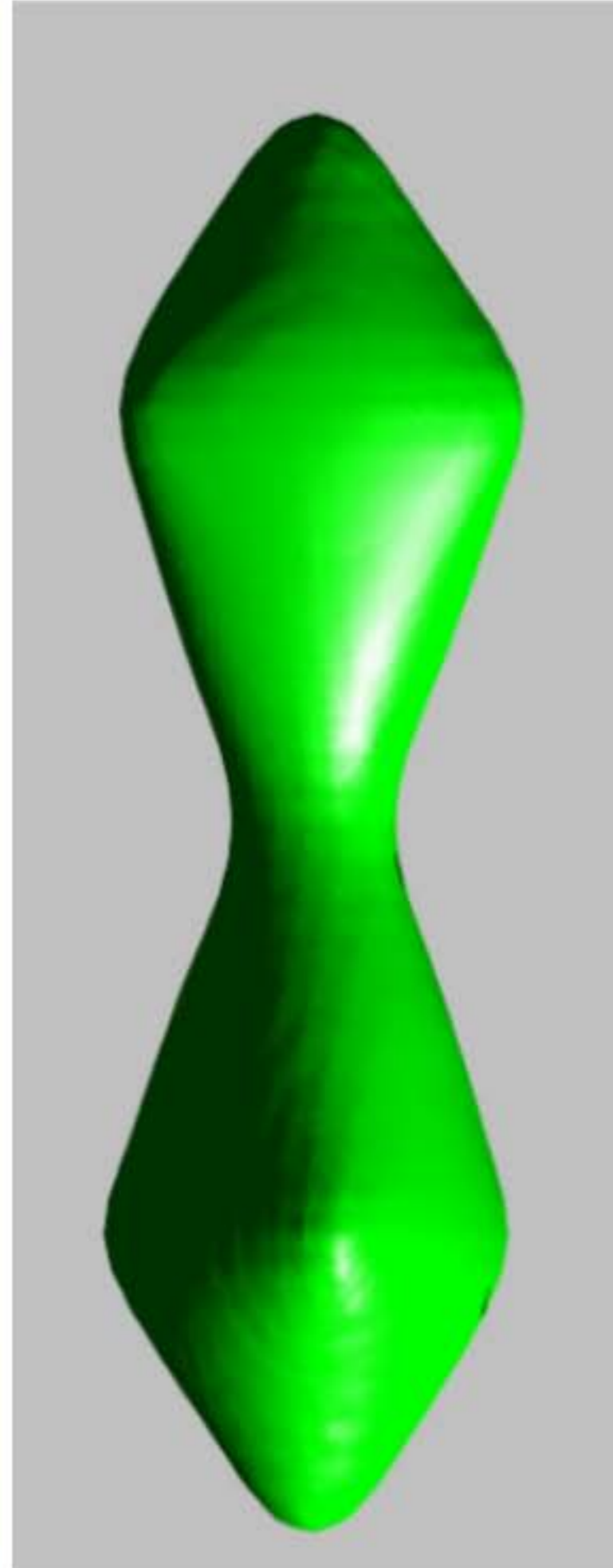
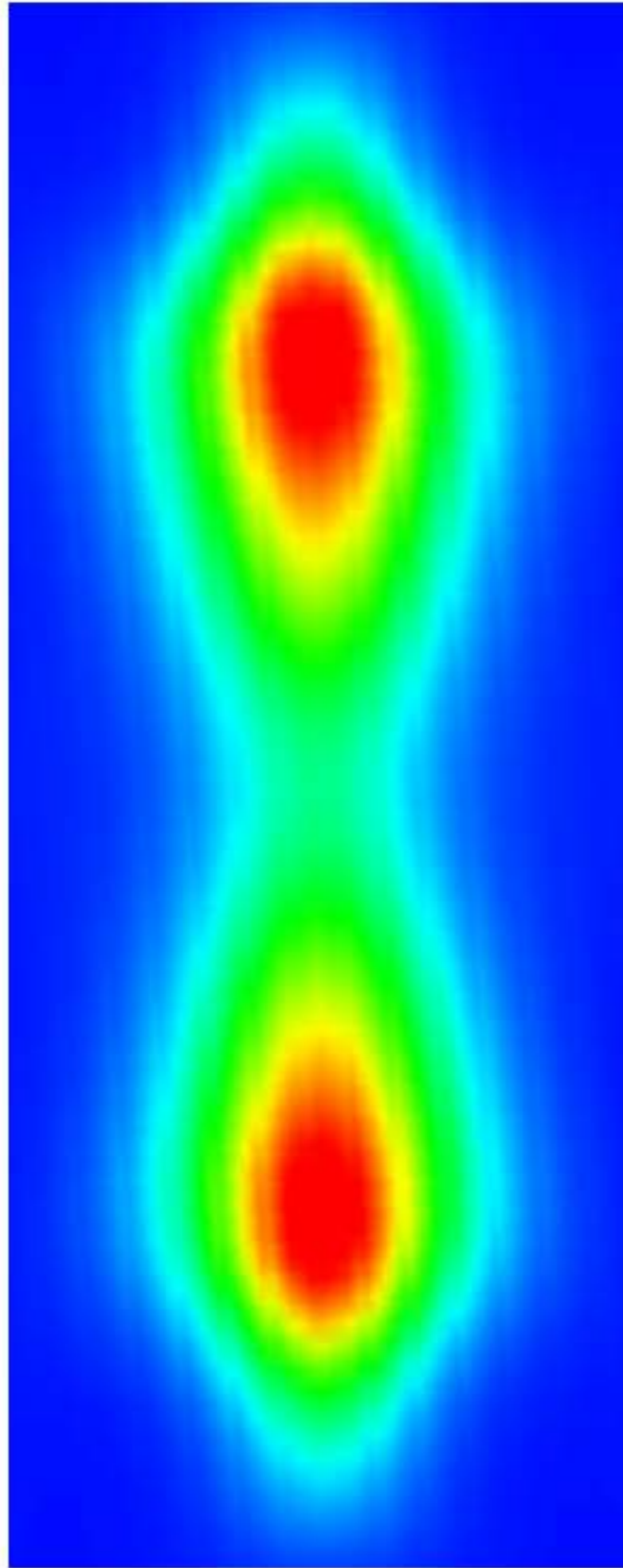
Figure 6: Schematic representation of $(\text{Ba}_2\text{Co}_8\text{O}_{14})^{2-}$ block (a) viewed along (001) and (b) viewed along (010)

Figure 7: Schematic representation of (a) $(\text{Ba}_2\text{Cl}_2)^{2+}$ block viewed along [010] and (b) structure reference fluorite viewed along [011]

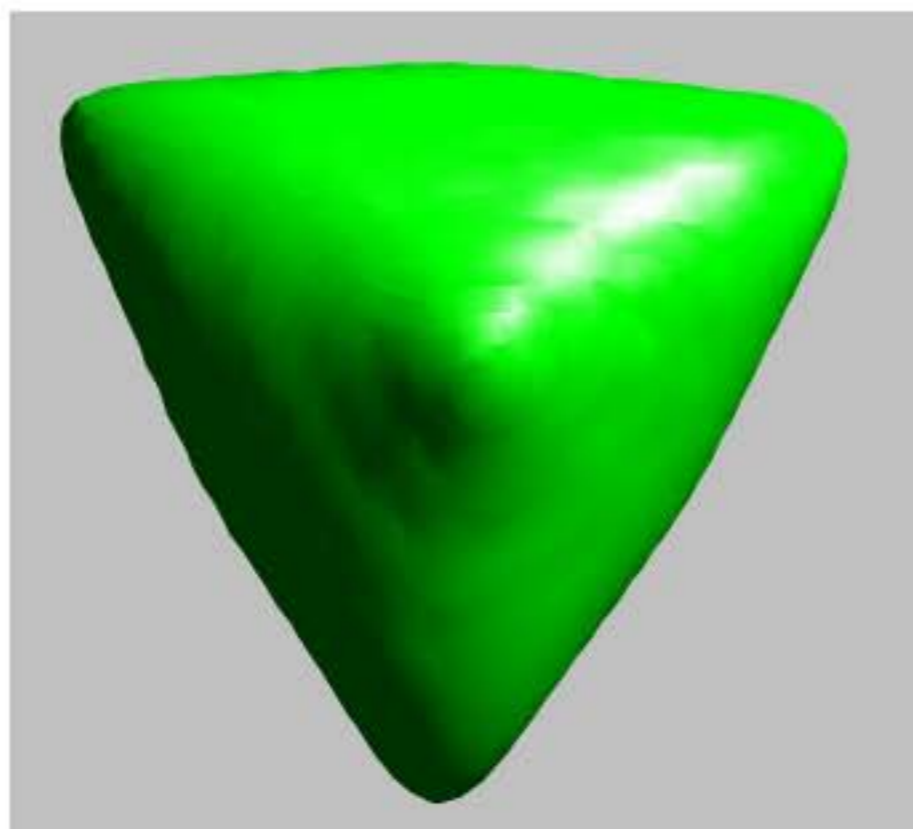
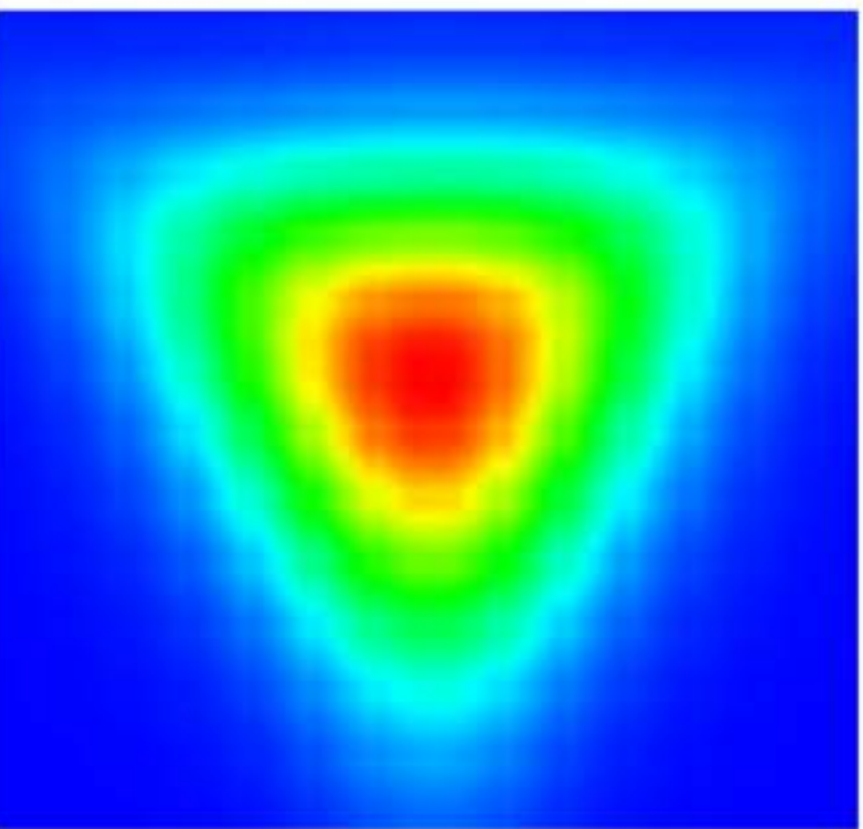
Figure 8: Two- and three-dimensional electron density (ED) images for (a) Cl(1) atom, (b) Br(1) atom and (c) Br(2) atom



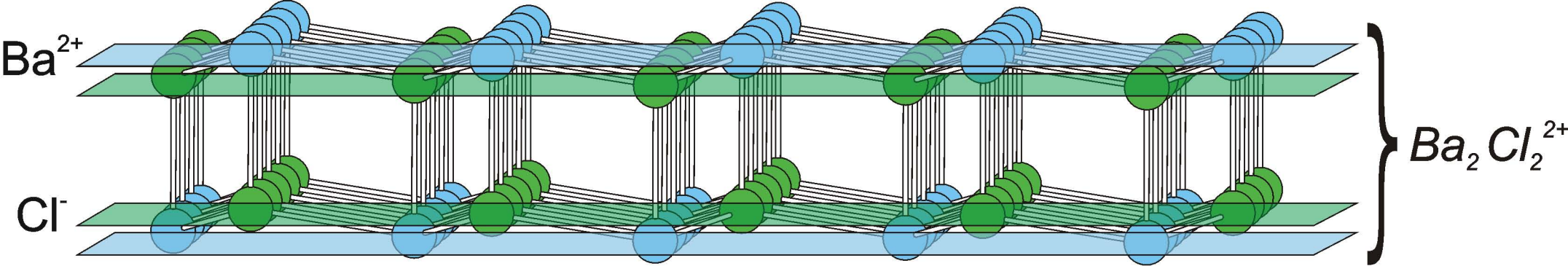
(a)



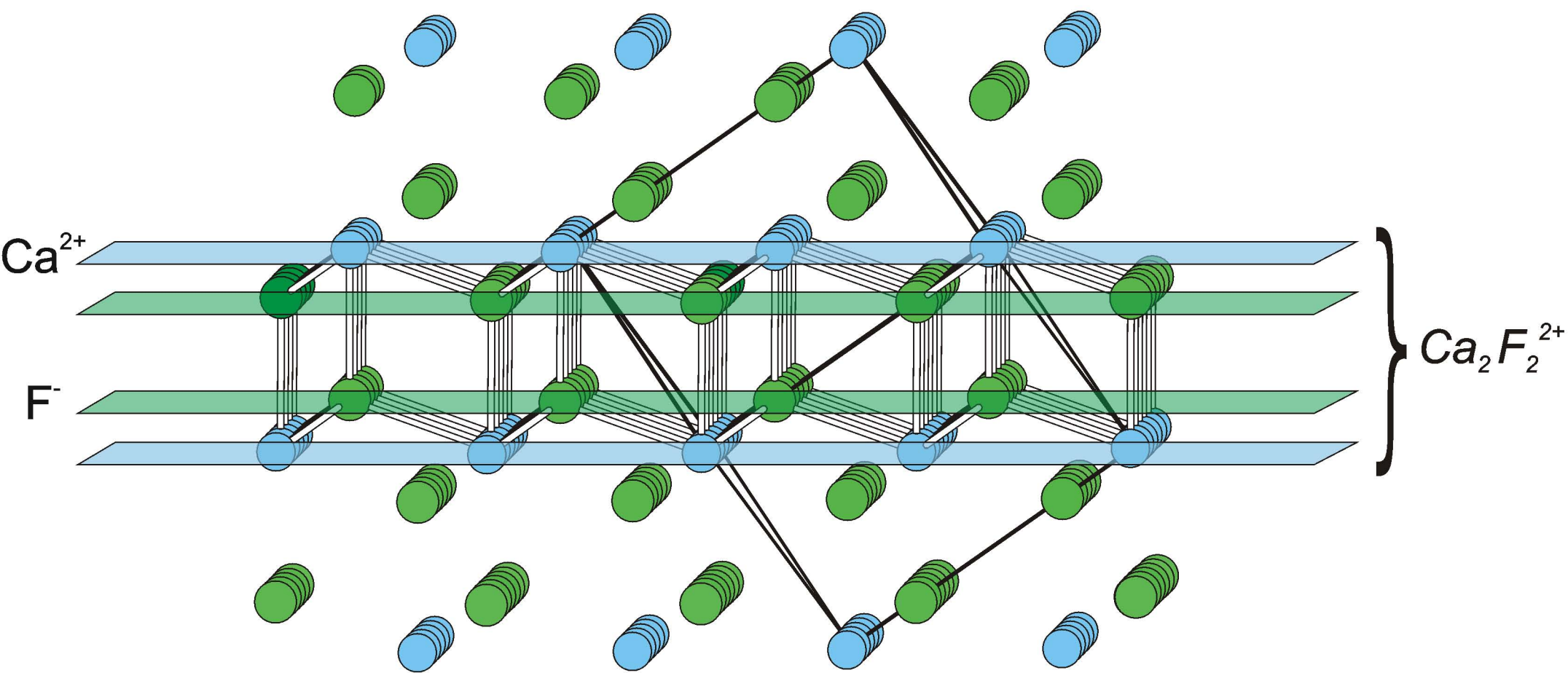
(c)



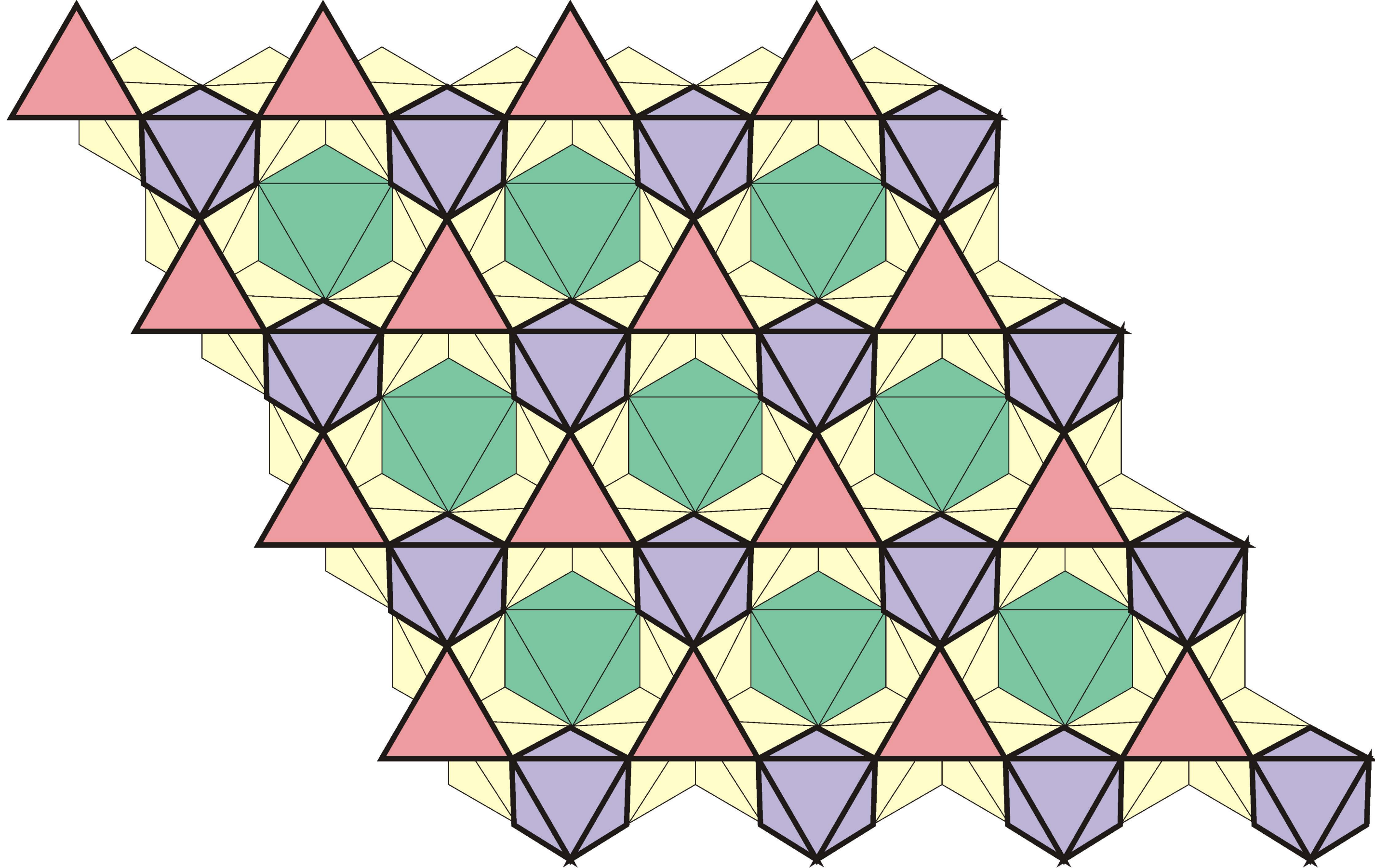
(b)



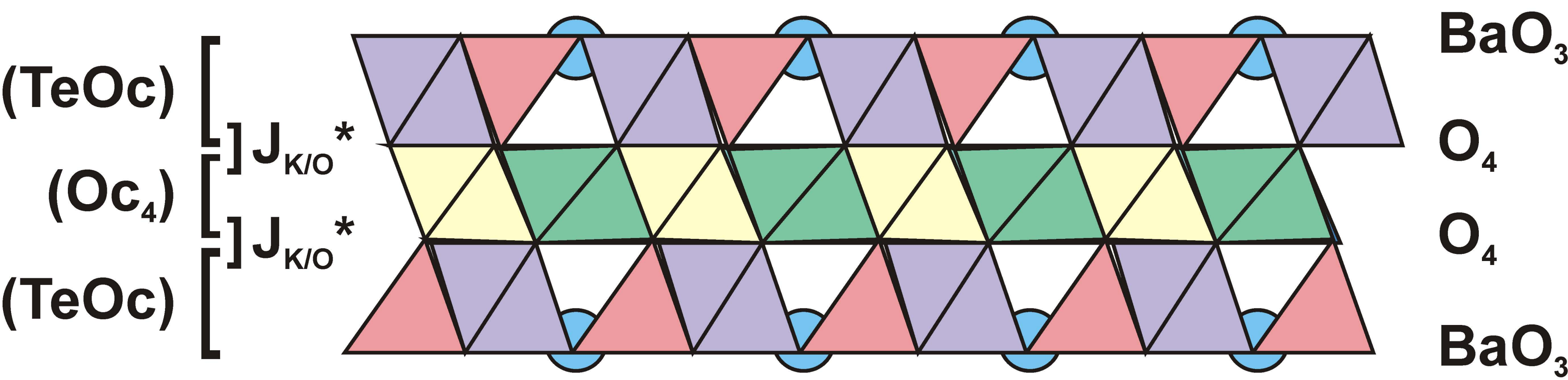
(a)



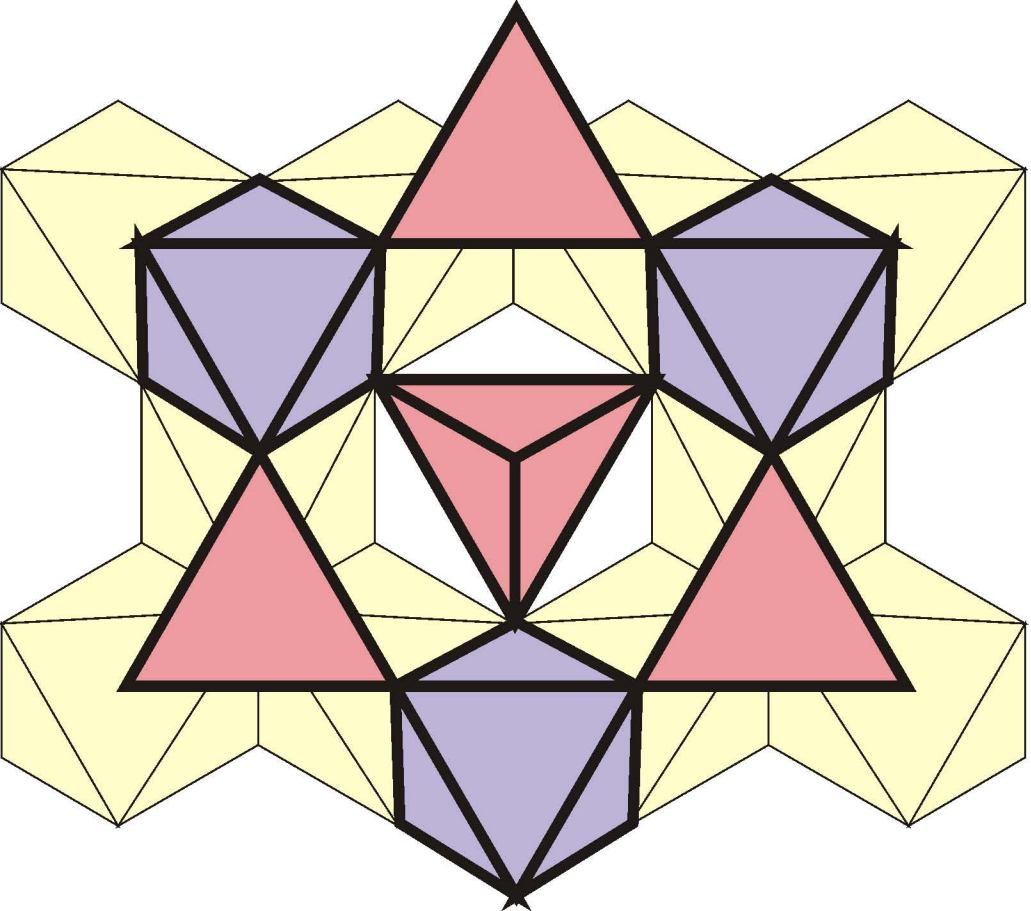
(b)



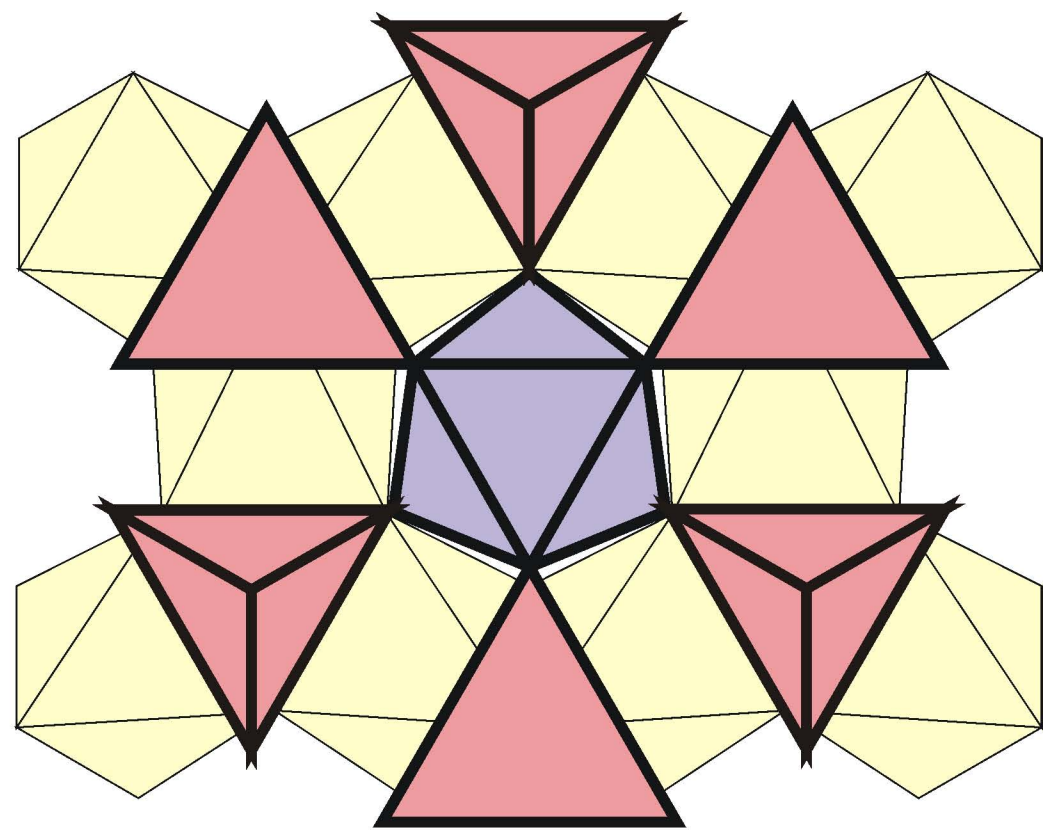
(a)



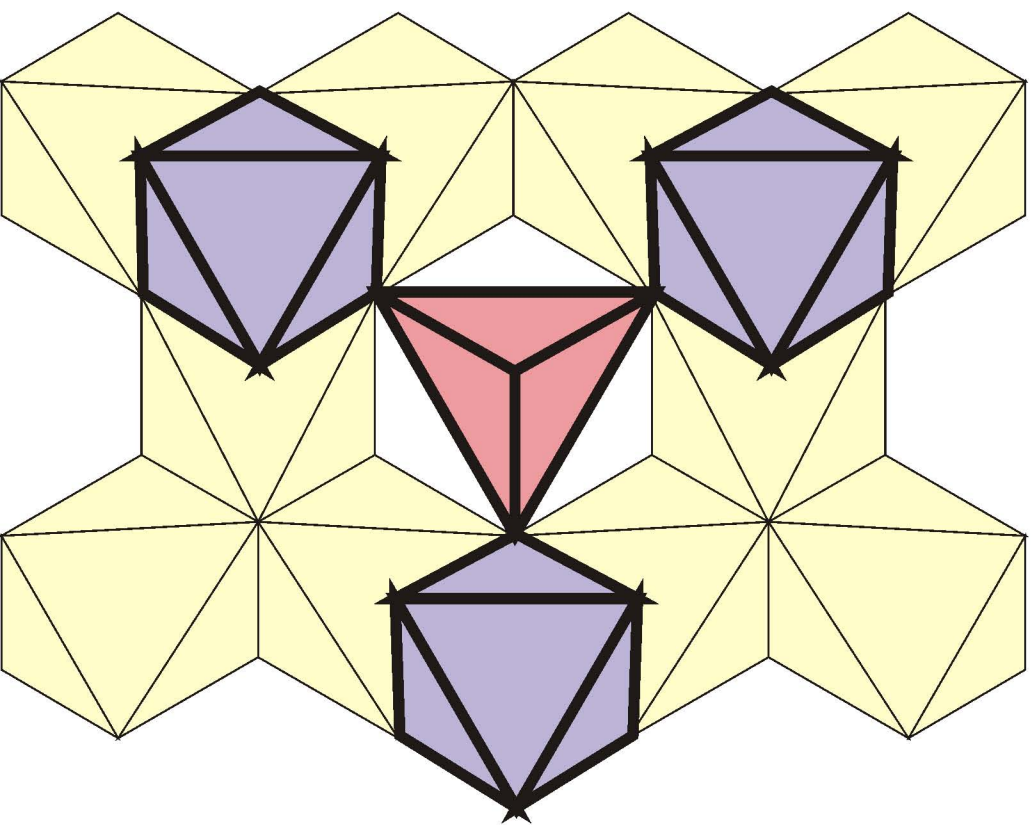
(b)



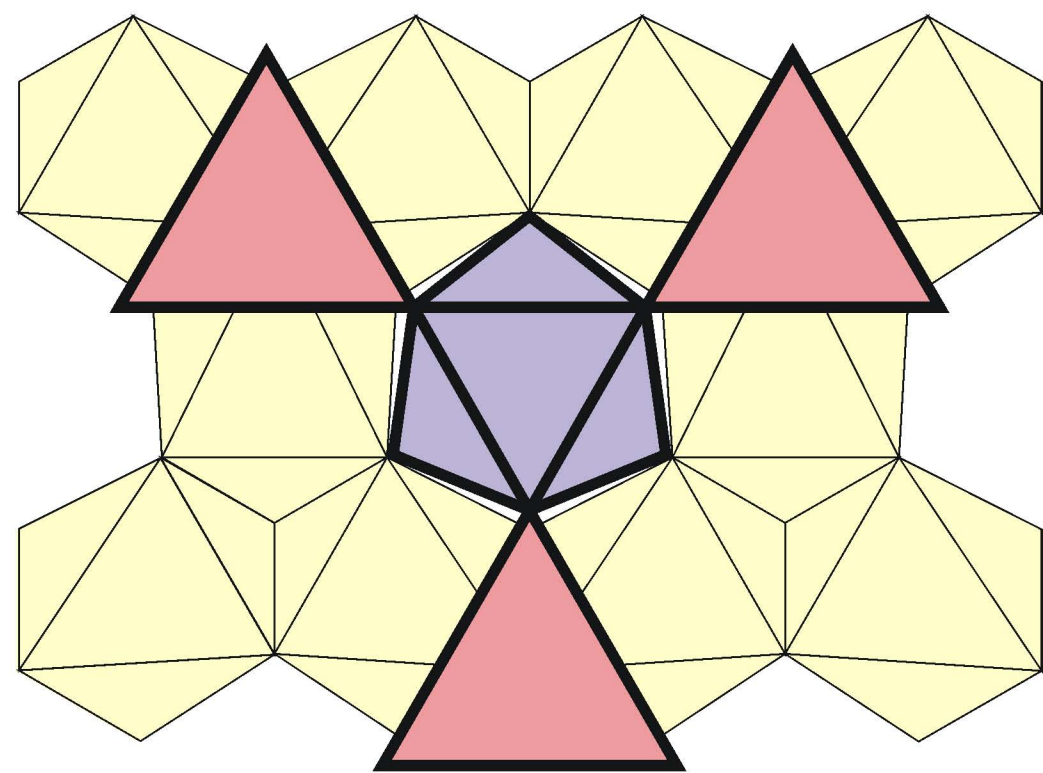
(a)



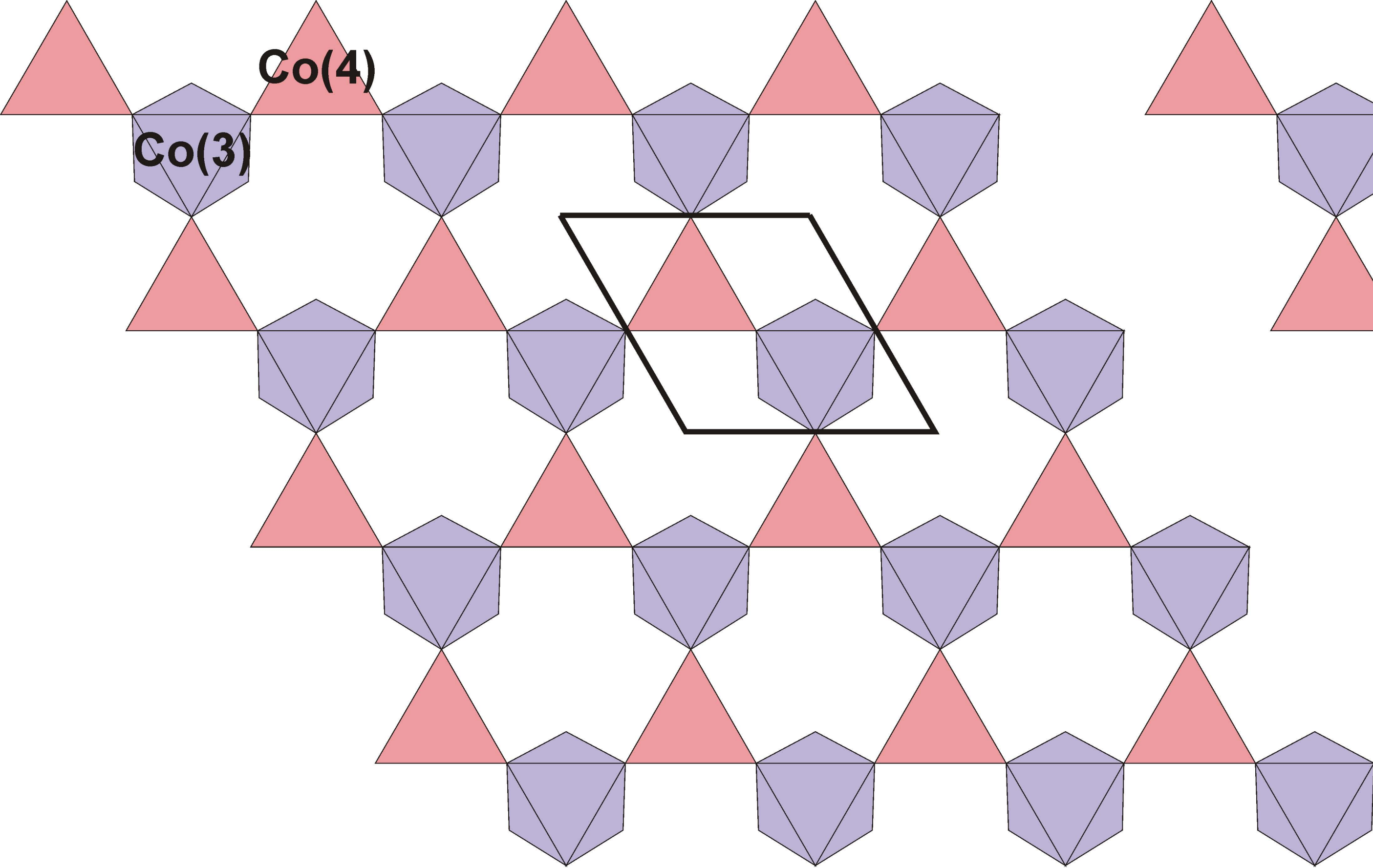
(b)



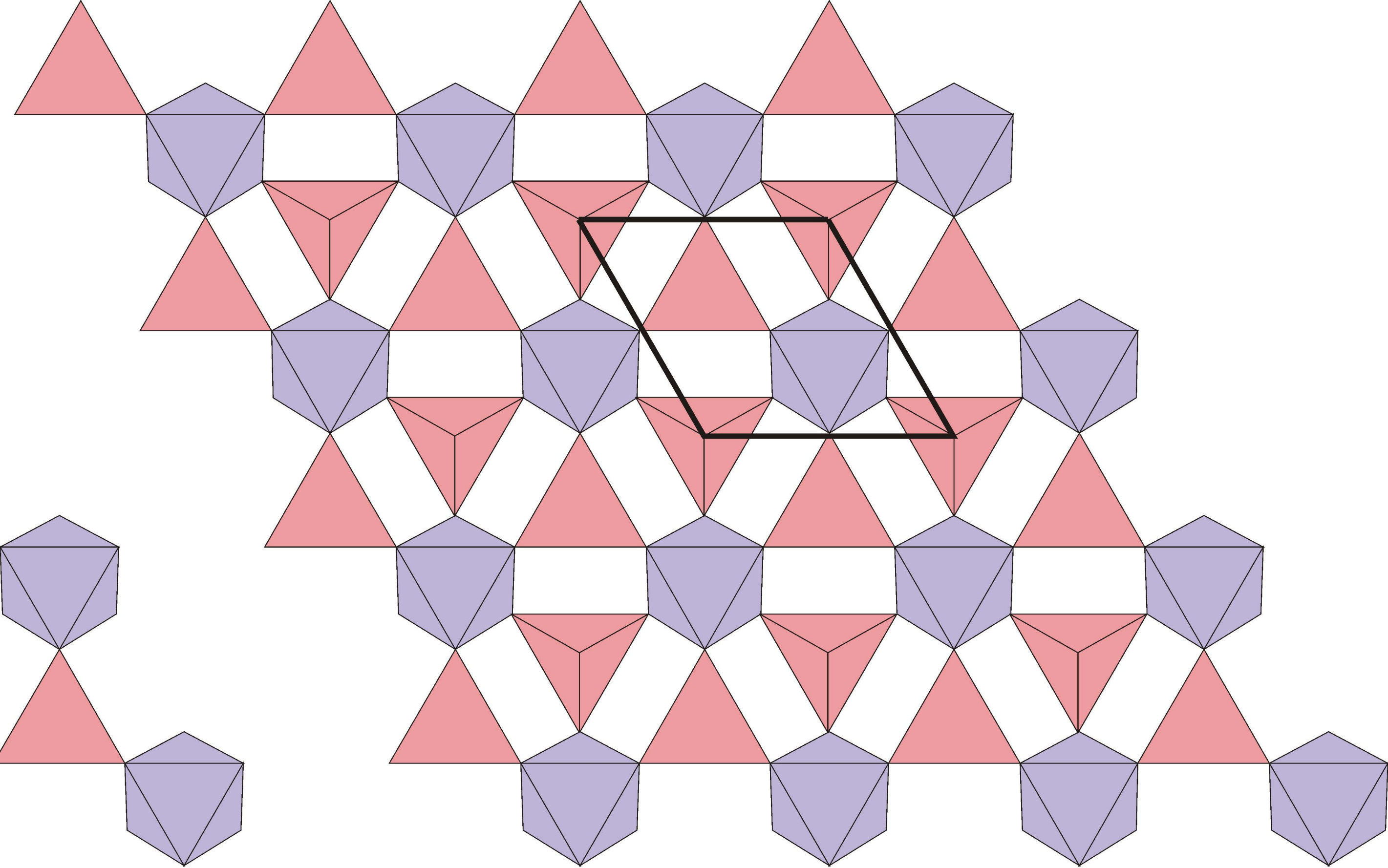
(c)



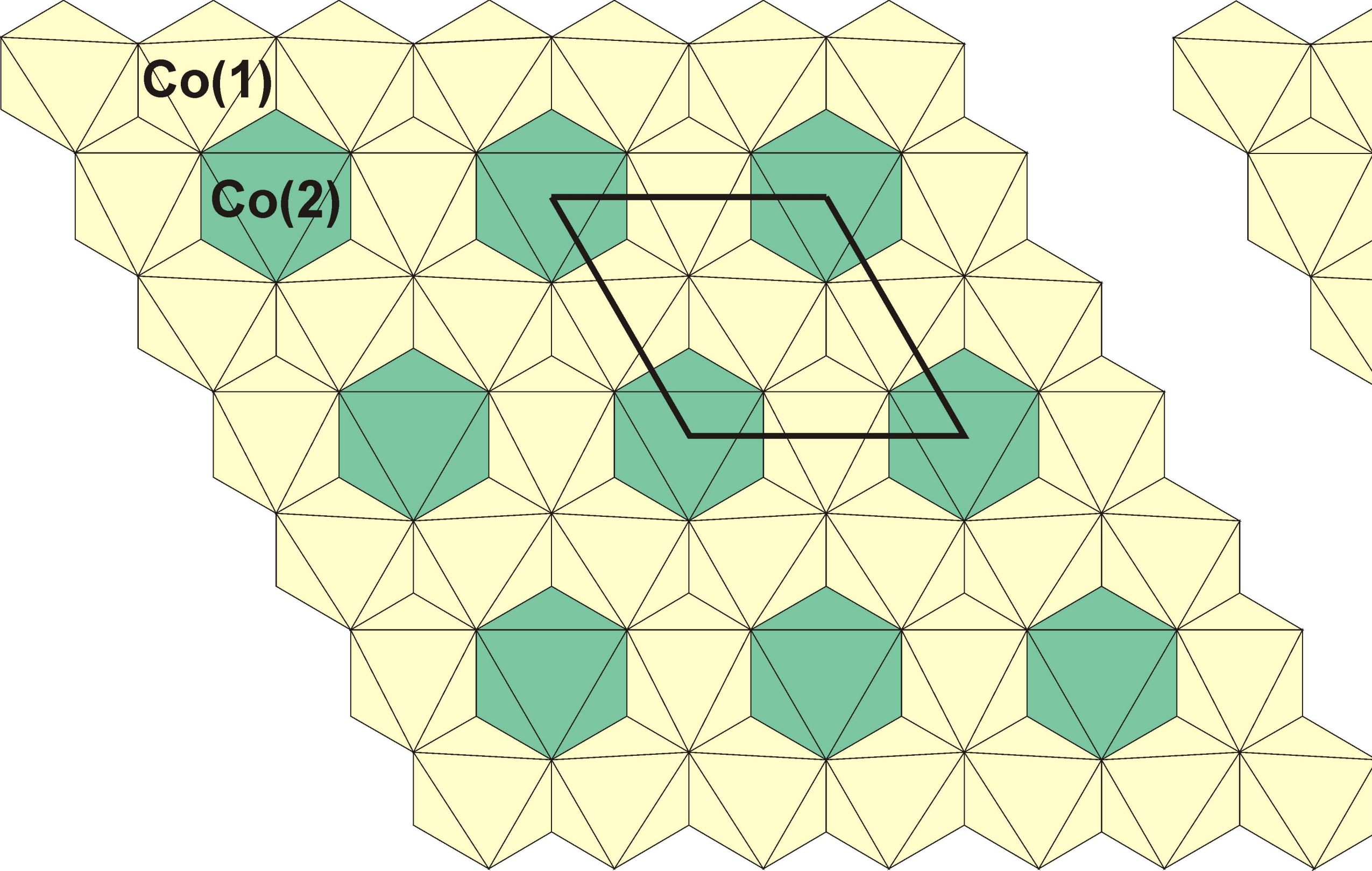
(d)



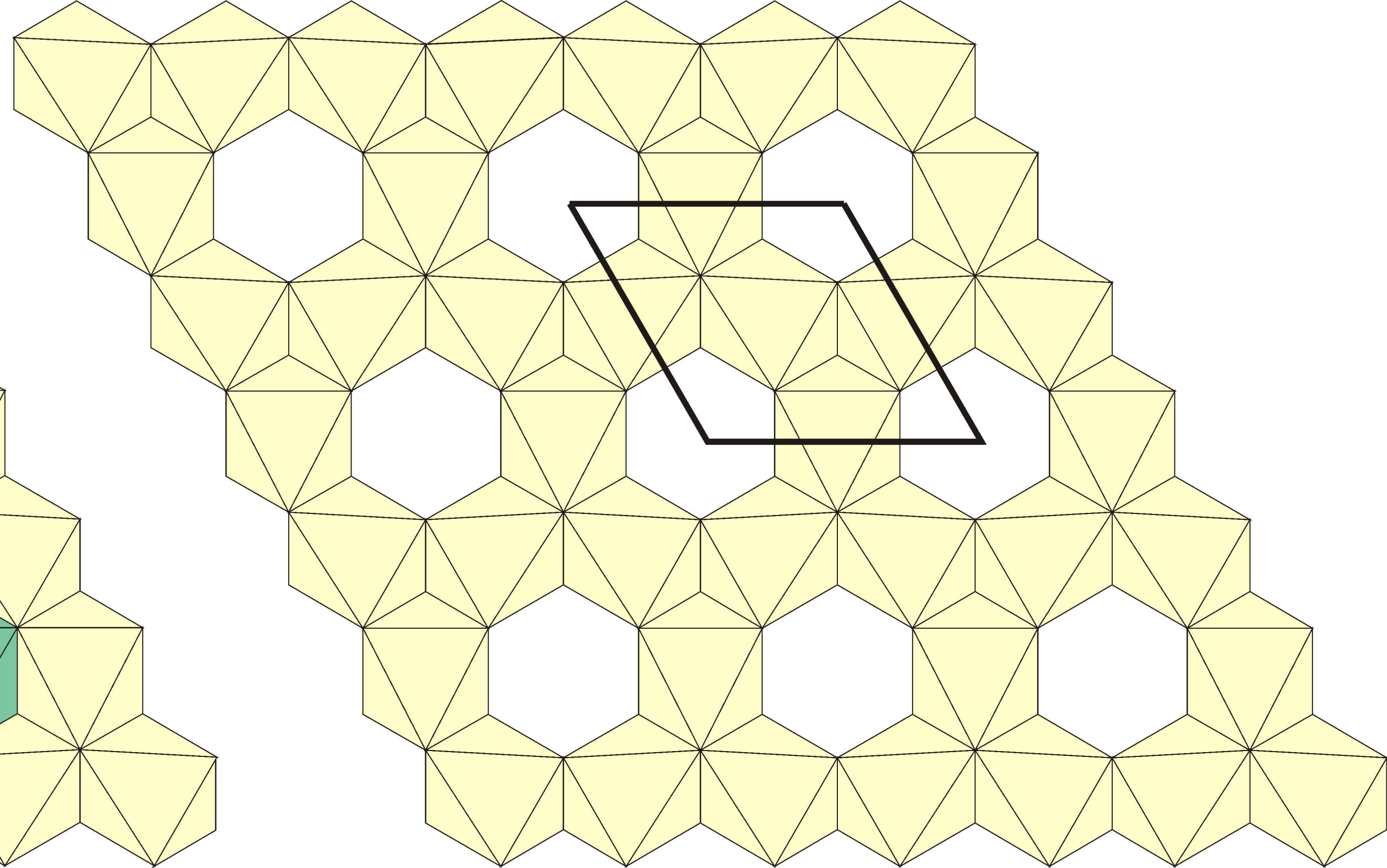
(a) - (TeOc) layer



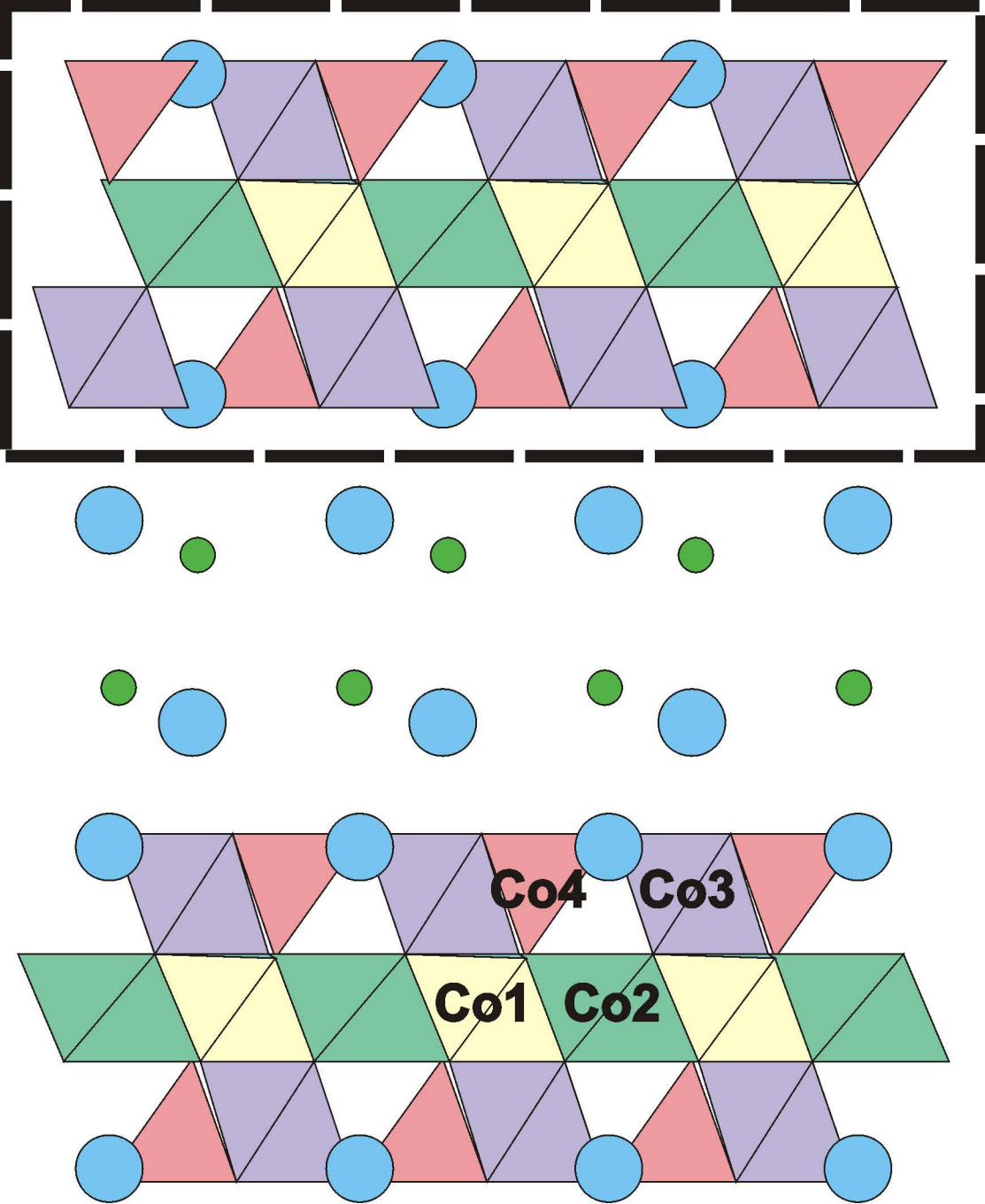
(b) - (Te_2Oc) layer



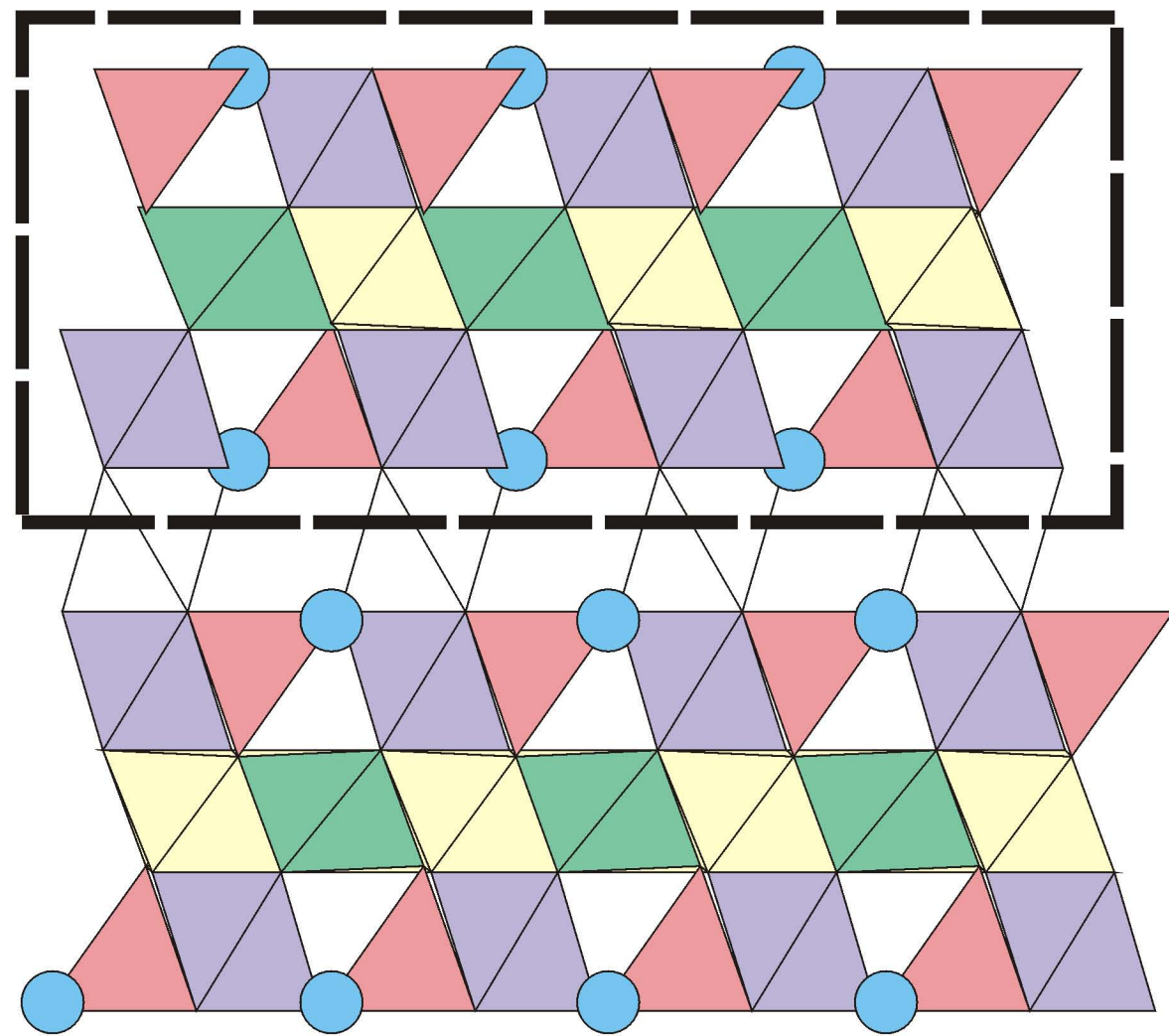
(a) - (Oc_4) layer



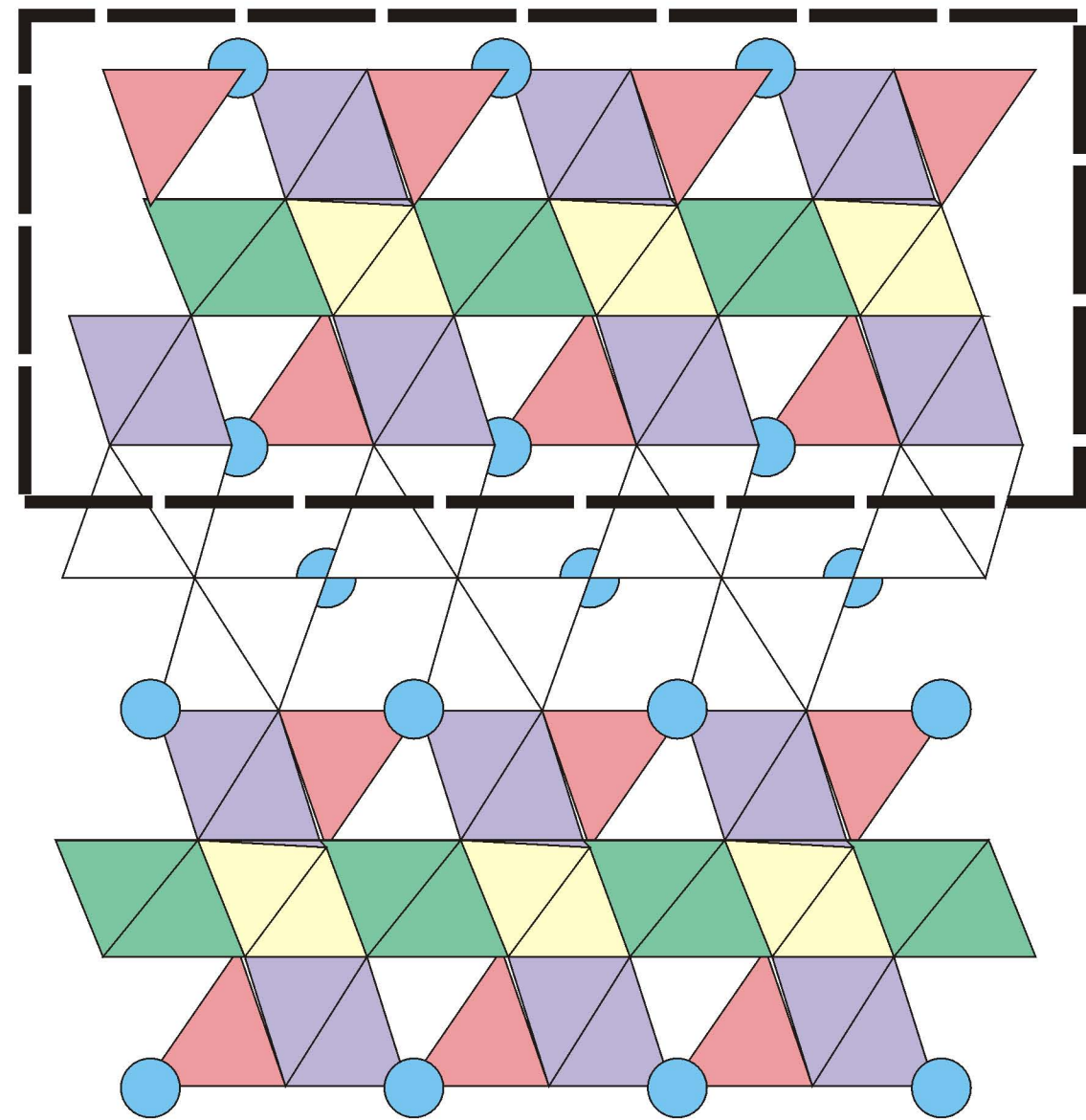
(b) - (Oc_3) layer



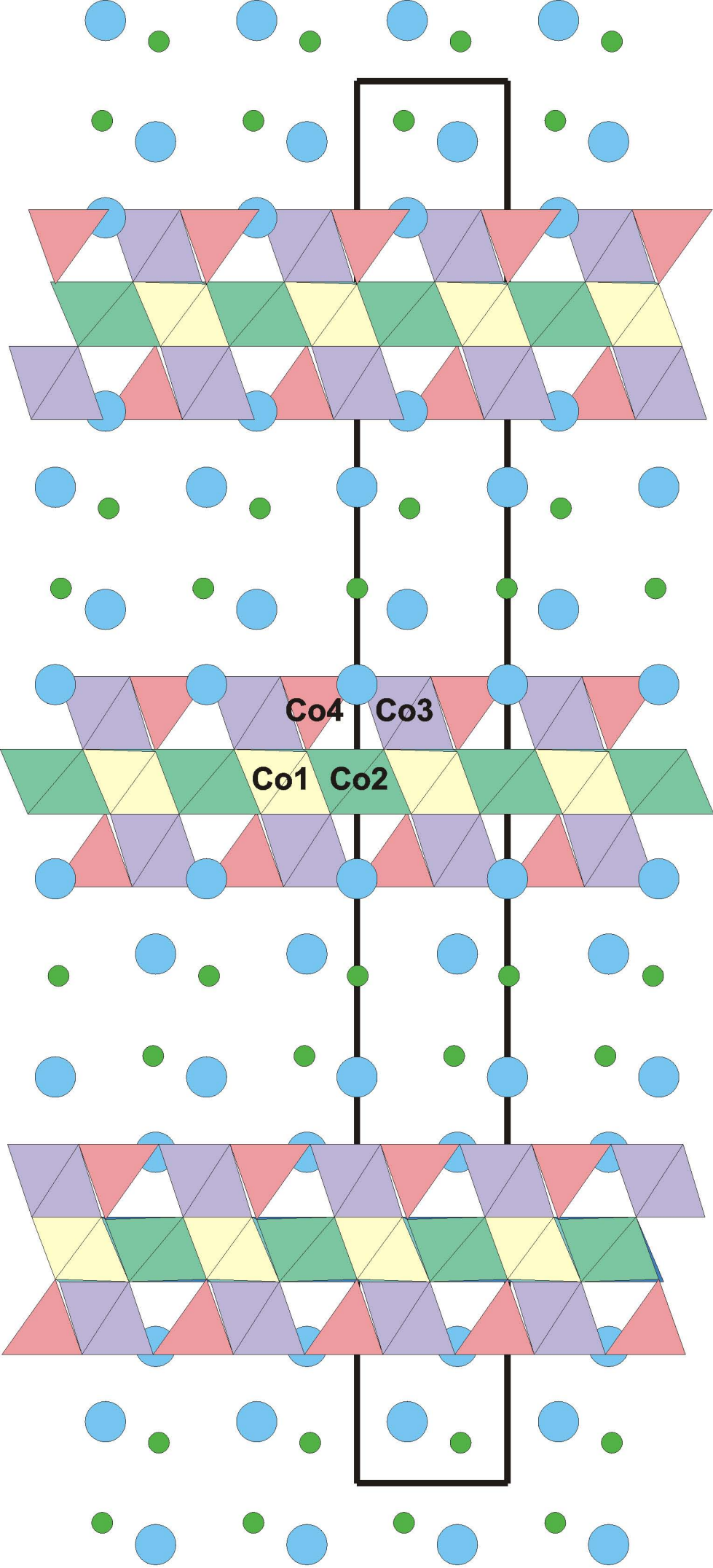
(a)



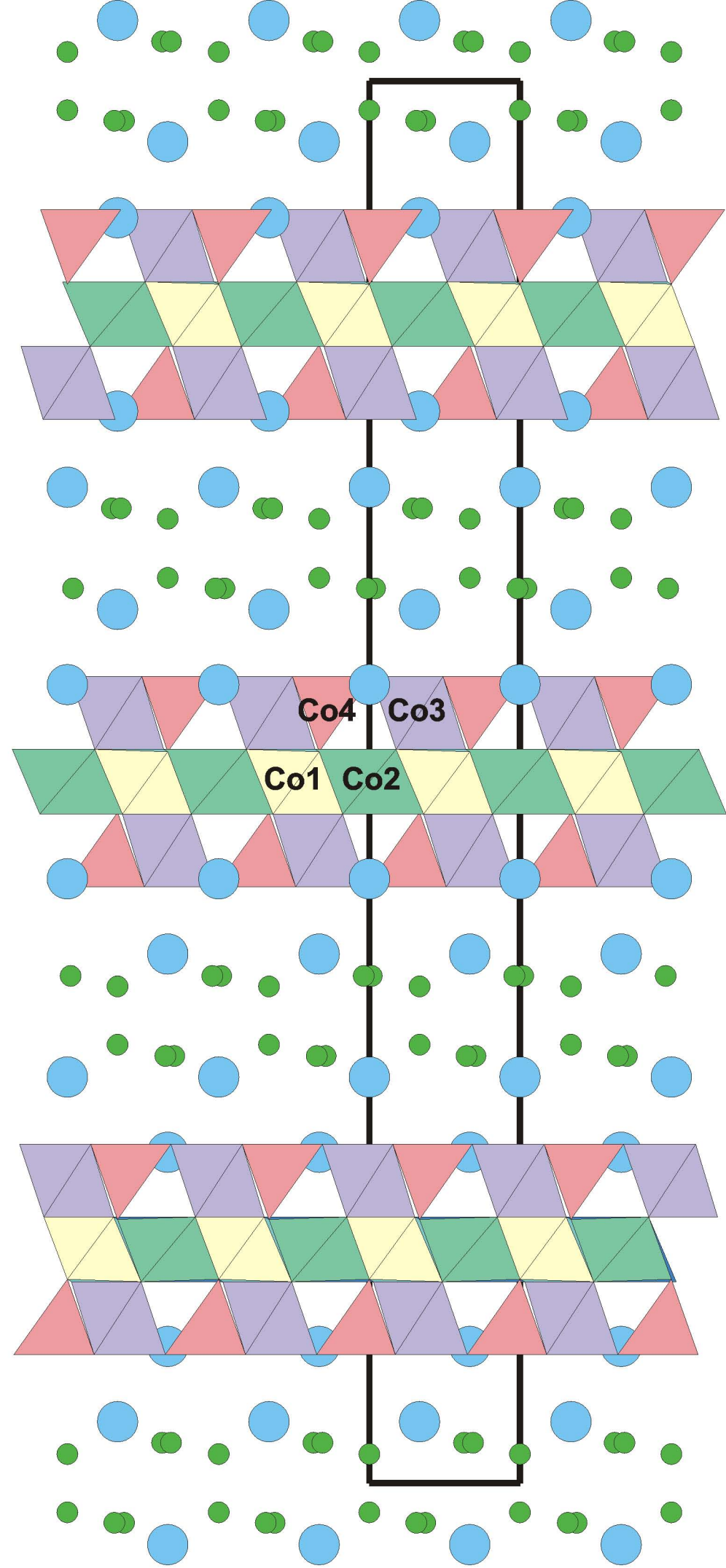
(b)



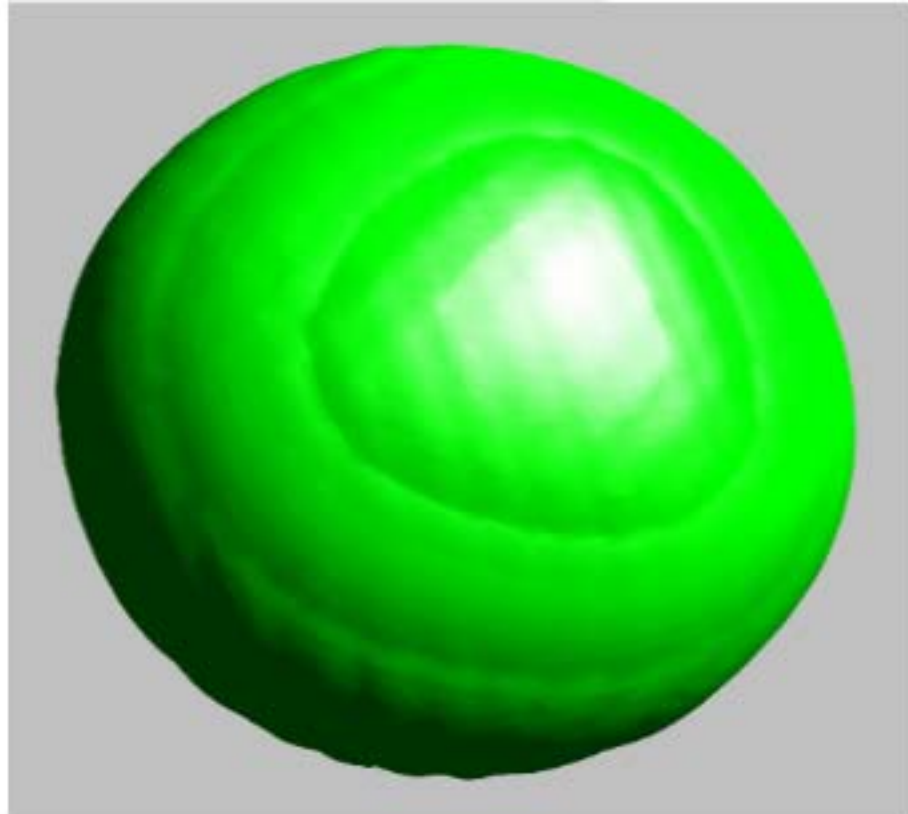
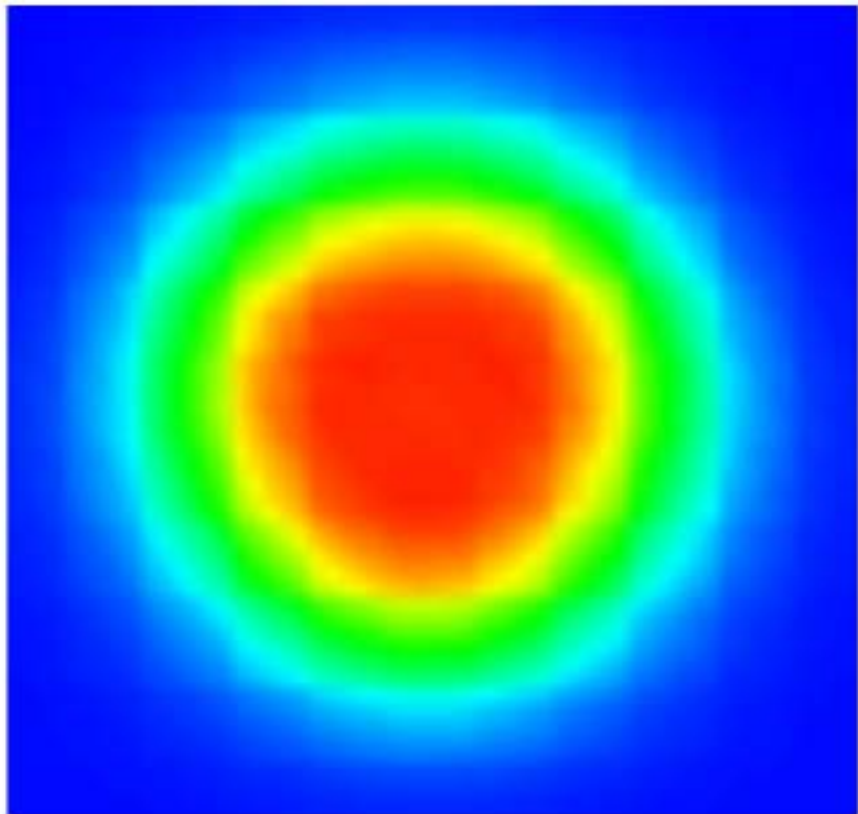
(c)



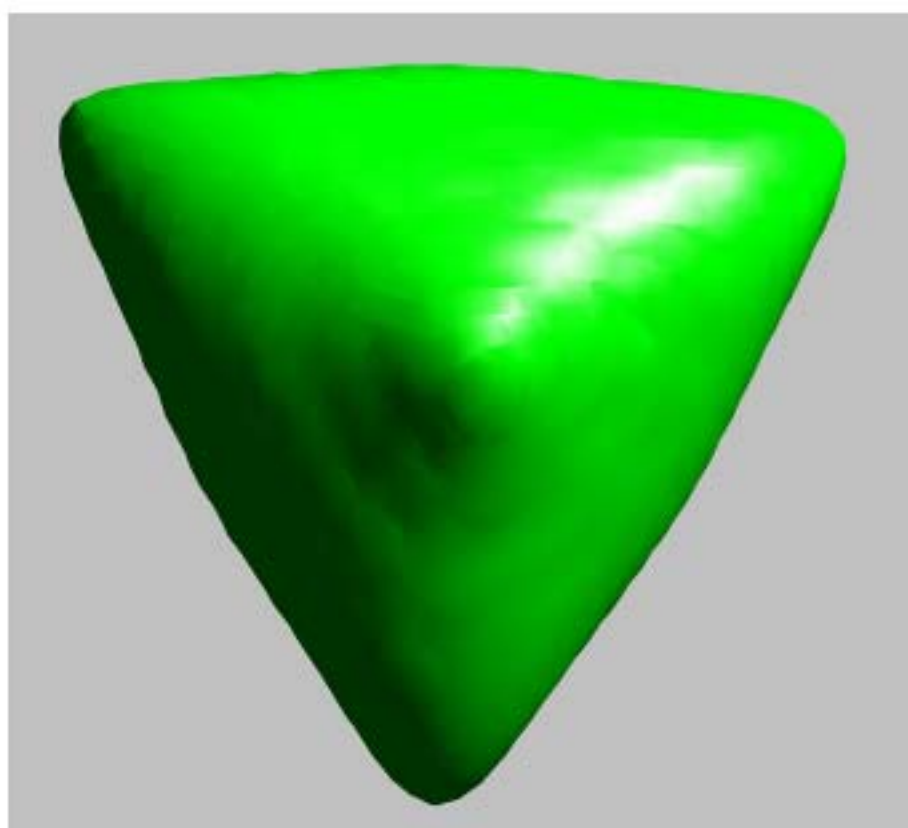
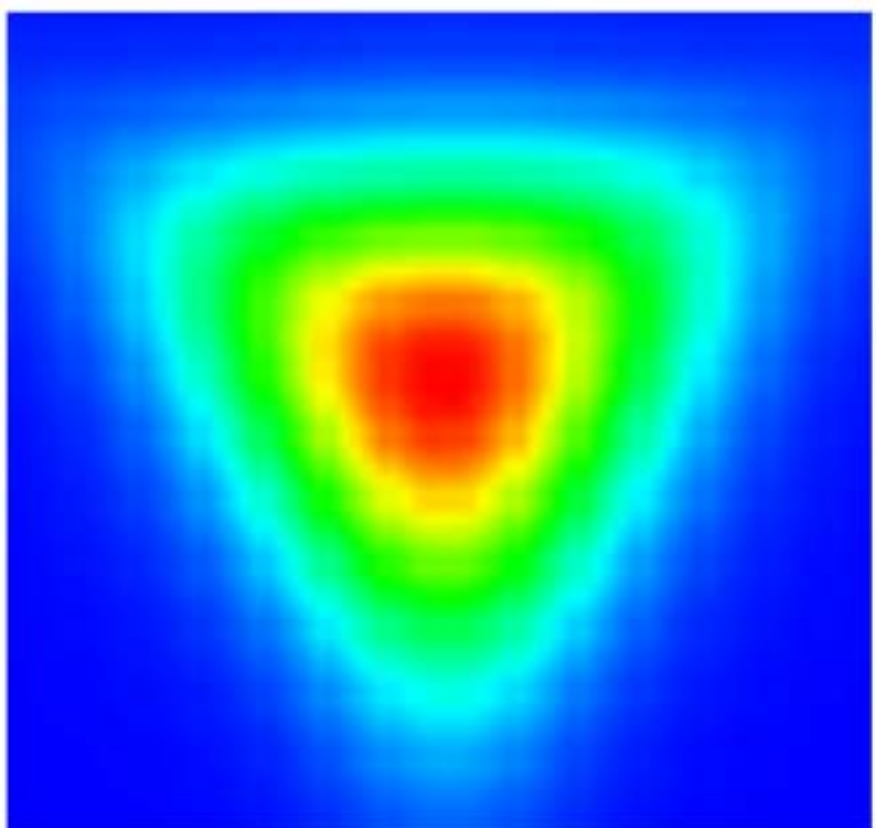
(a)



(b)



(a)



(b)