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Combining selective sequential extractions, X-Ray Absorption Spectroscopy, and X-Ray Powder Diffraction for Cu (II) speciation in soil and mineral phases

Tatiana M. Minkina [a,*], Dina G. Nevidomskaya [a], Alexander V. Soldatov [b],
David L. Pinskii [c], Fariz Mikailsoy [d], Victoria S. Tsitsuashvili [b],
Tatiana V. Bauer [a], Victoria A. Shuvaeva [e]

[a] Southern Federal University, Academy of Biology and Biotechnology of D.I. Ivanovsky, Rostov-on-Don, Russia
[b] Southern Federal University, International Research Center "Smart Materials", Rostov-on-Don, Russia
[c] Institute of Physicochemistry and Biological Problems of Soil Sciences Russian Academy of Sciences, Pushchino, Moscow Region, Russia
[d] University of Iğdır, Agricultural Faculty, Department of Soil Science and Plant Nutrition, Iğdır, Turkey
[e] Southern Federal University, Research Institute of Physics, Rostov-on-Don, Russia

Article Info

Abstract

Interaction of Cu (II) ions with the matrix of soil and mineral phases of layered silicates was assessed by the Miller method of selective sequential fractionation and a set of synchrotron X-ray methods, including X-ray powder diffraction (XRD) and X-ray absorption spectroscopy (XANES). It was shown that the input of Cu into Calcic Chernozem in the form of monoxide (CuO) and salt ($Cu(NO_3)_2$) affected the transformation of Cu compounds and their affinity for metal-bearing phases. It was found that the contamination of soil with a soluble Cu(II) salt increased the bioavailability of the metal and the role of organic matter and Fe oxides in the fixation and retention of Cu. During the incubation of soil with Cu monoxide, the content of the metal in the residual fractions increased, which was related to the possible entry of Cu in the form of isomorphic impurities into silicates, as well as to the incomplete dissolution of exogenic compounds at the high level of their input into the soil. A mechanism for the structural transformation of minerals was revealed, which showed that ion exchange processes result in the sorption of Cu (II) ions from the saturated solution by active sites on the internal surface of the lattice of dioctahedral aluminosilicates. Surface hydroxyls at the octahedral aluminum atom play the main role. X-ray diagnostics revealed that excess Cu(II) ions are removed from the system due to the formation and precipitation of coarsely crystalline $Cu(NO_3)(OH)_3$.

Keywords: Cu (II) ions, calcic chernozem, mineral phases, sequential fractionation, XRD, XANES Spectroscopy.

Introduction

The bioavailability of metals is closely related to their forms of occurrence. Therefore, studies of soil contamination aimed at obtaining objective information about metal speciation become of special importance (Minkina et al., 2010). The complexity of the occurrence forms of metals and metalloids is most manifested in highly dynamic, physically and chemically heterogeneous ecological systems like soils, bottom

sediments, and sewage sludge (Hesterberg et al., 2011). Analytical methods used to assess metal compounds are usually suitable for the study of limited combinations of metals and metalloids in environmental objects. The mechanical transference of extraction systems developed for background soils introduces additional uncertainties and errors in the study of contaminated soils. The proportions of phosphates, sulfides, and arsenates, for which there are no adequate extractants, increase in industrially contaminated soils (Orlov et al., 2005). Chemical reagents should provide the maximum completeness and selectivity of extraction for target metals. However, this is almost inaccessible for such a complex polydisperse heterogeneous system as the soil because of the internal spatial heterogeneity of soil samples. The determination of heavy metals (HMs) and metalloids in soils should evolve toward direct methods ensuring selectivity and sensitivity for the local structures of numerous elements; low detection limits; high spatial resolution; and a simple procedure of sample preparation, which makes these methods universal and accurate in studying the elemental composition of pollutants (Gräfe et al., 2014; Minkina et al., 2016).

The aim of this work was to study relationships between Cu(II) ions and components of soil organomineral matrix by X-ray absorption spectroscopy (XANES) and X-ray powder diffraction (XRD) using synchrotron radiation and, selective sequential fractionation.

Material and Methods

Objects of study included samples from the humus-accumulative A_1 horizon of Calcic Chernozem (FAO, 2006) collected in the Persianovskaya Step Specially Protected Natural Territory, Rostov oblast, Russia. The soil had the following properties: C_{org} 3.7%, $CaCO_3$ 0.4%, pH_{H_2O} 7.6; exchangeable bases (mM(+)/100 g): Ca^{2+} 31.0, Mg^{2+} 6.0, Na^+, 0.06; physical clay 63.6%; clay 28.1%. The content of total Cu in the samples was determined by synchrotron radiation X-ray fluorescence analysis (SR XRF). Chemical compositions of the mineral component of Chernozem and the phases of layered silicates were determined using the procedure for measuring the mass fractions of element oxides in powdered samples by the X-ray fluorescence method on a MAKS-GV spectroscane.

The mineralogy of the clay and fine silt fractions from the humus-accumulative horizon of Calcic Chernozem is characterized by the following phase composition of layered silicates: the contents of illite, labile silicates, and kaolinite are 51–54 and 51–60, 23–27 and 12–27, and 22–23 and 22–28% in the clay and fine silt fractions, respectively. The fine silt fraction also contains micas, amorphous silica, and crystallized iron and aluminum oxides and hydroxides (Kryshchenko and Kuznetsov, 2003; Nevidomskaya et al., 2016).

To study the effect of organomineral matrix on the sorption of Cu^{2+} ions, a model laboratory experiment has been established under controlled conditions. The soil selected for the experiment was air-dried, triturated using a pestle with a rubber head, and sieved through a 1-mm sieve. Dry compounds of Cu ($Cu(NO_3)_2$ and CuO) were added to the soil at a rate of 2000 mg/kg. The soil was thoroughly mixed, wetted, and incubated for 3 years at 60% of the maximum water capacity. Experiments were performed in triplicates. Analogous procedures but without addition of metal were performed with the control sample.

After the end of incubation (3 years layer), an average sample was taken from each pot for analysis. The soil was brought to the dry state.

Samples of separate mineral phases (montmorillonite, kaolinite, hydromuscovite, and gibbsite) were saturated with Cu^{2+} ions. For this purpose, the studied samples were put into a saturated $Cu(NO_3)_2$ solution. The solution was changed twice a day for a week. The solution pH was maintained constant at 7.0 in the presence of CuO and 3.9 in the presence of $Cu(NO_3)_2$. After a week, the preparation was removed from the solution, dried, and ground.

Sequential extraction

The composition of Cu compounds in the soil was determined by the Miller method of sequential fractionation (Miller et al., 1986) modified by Berti and Jacobs (1996). The chemical fractionation extracted the following Cu compounds (Table 1): water-soluble, exchangeable, and acid-soluble; bound to Mn oxides, organic matter, and amorphous and crystalline Fe oxides; and insoluble (bound to aluminosilicates, or residual) ones. Analysis of Cu content in soil extracts was performed by atomic absorption spectrophotometry (AAS).

Table 1. Sequential fractionation of heavy metals by the Miller scheme (Miller et al., 1986) modified by Berti and Jacobs (1996) for 1 g sample

Fraction	Soil : solution ratio	Extraction conditions	Extractant
Water-soluble	1 : 10	Shaking at room temperature for 16 h	Distilled water
Exchangeable	1 : 10	Shaking at room temperature for 8 h	0.5 M $Ca(NO_3)_2$, pH 7.0
Acid-soluble	1 : 10	Shaking at room temperature for 8 h	0.44 M CH_3COOH, pH 2.5
Bound to Mn oxides	1 : 14	Shaking at room temperature for 30 min	0.1 M $NH_2OH \cdot HCl$ + 0.01 M HNO_3
Bound to organic matter	1 : 14	Shaking at room temperature for 24 h	0.1 M $Na_4P_2O_7$
Bound to amorphous Fe oxides	1 : 14	Shaking in the dark for 4 h	0.175 M $(NH_4)_2C_2O_4$ + 0.1 $MH_2C_2O_4$
Bound to crystalline Fe oxides	1 : 14	Placed in a boiling water bath under periodical shaking for 5 h	0.175 M $(NH_4)_2C_2O_4$ + 0.1 $MH_2C_2O_4$
Connected with silicates (residual)	1 : 25	Evaporation	Extract of HF + $HClO_4$ from the residual fraction

Soil samples were also analyzed by X-ray powder diffraction and X-ray absorption spectroscopy at the Structural Material Science station on the 1.3b channel of a synchrotron radiation source of the National Research Center "Kurchatov Institute" (Chernyshov et al., 2009). A 1.7 T bend magnet of the Siberia-2 storage ring is the source of synchrotron radiation. The electron beam energy is 2.5 GeV; the average current is 120 mA.

X-ray powder diffraction.

Diffraction studies of monochromatic synchrotron X-ray radiation (λ = 0.68886 Å, Si monochromator) were performed in transmission geometry using a Fujifilm Imaging Plate two-coordinate detector at 0.68886 Å. X-ray diffraction patterns were recorded in integrated mode at 20°C. The time of sample exposure was about 15 min. A silicon standard (NIST SRM 640C) was used for the angular calibration of the scale. The use of high-intensity monochromatic synchrotron radiation in combination with a two-coordinate detector and a Si monochromator significantly improves the intensity and resolution of diffraction patterns compared to the conventional X-ray diffractometry.

X-ray absorption spectroscopy.

Experimental Cu K-edge X-ray absorption near edge structure (XANES) spectra (~899–8995 eV) were measured at room temperature in fluorescence mode. A two-crystal Si(111) monochromator with the energy resolution $\Delta E/E \sim 2 \cdot 10^{-4}$ was used to monochromate the X-ray radiation. The obtained spectra were processed using standard procedures for noise discrimination and normalization by the K-edge jump. First-derivative XANES spectra were analyzed to specify information about the state of Cu(II) ions and reveal the differences in the analyzed samples that escaped detection during the analysis of XANES spectra. Along with the experimental XANES spectra, experimental spectra of the original copper-containing compound were also studied.

Results and Discussion

Fractionation of Cu compounds by the Miller method showed (Figure 1) that Cu compounds in the fraction bound to silicates dominate in the uncontaminated Chernozem (60 and 67% of the sum of total fractions). This is related to the regional biogeochemical features of the microelement composition of soils in Rostov oblast and the mineralogy of parent rocks (Akimtsev et al., 1962).

Copper compounds have low mobility in the uncontaminated soil. The relative content of Cu in the first three fractions does not exceed 1.5%, and the most mobile exchangeable forms compose only 0.4%. It is known that Cu is an organophilic element (Vodyanitskii, 2008; Ponizovskii et al., 1999); therefore, the organic matter fraction is characterized by a high Cu content. Perelomov (2001) and Kosheleva et al. (2002) confirmed that organic matter (especially high-molecular-weight humic acids) has higher effect on the fixation of Cu than carbonates and hydroxides. Copper compounds in the original soil are distributed as follows: silicate-bound (residual) fraction > organic matter-bound fraction > crystalline Fe-bound fraction > amorphous Fe-bound fraction >Mn oxide-bound fraction > acid-soluble fraction > exchangeable fraction ~ water-soluble fraction.
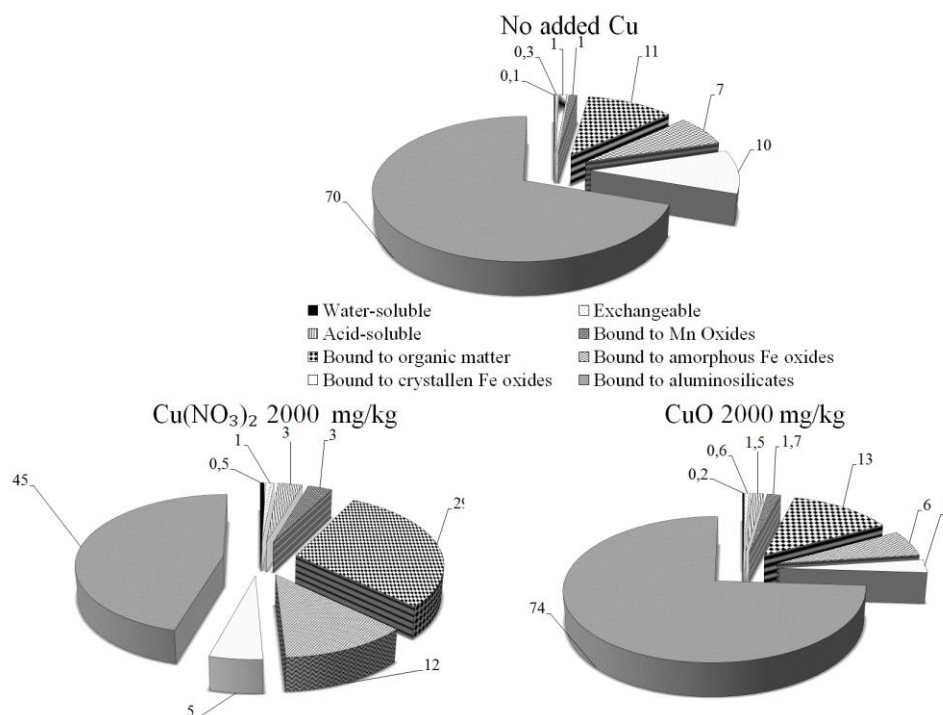
Figure 1. Distribution of Cu among fractions in the original Calcic Chernozem and that contaminated with $Cu(NO_3)_2$ and CuO from the Miller method, % of the sum of fractions

The artificial contamination of soil with Cu increases the absolute contents of all its compounds (Figure 1) and affects their distribution among the soil fractions. The proportion of the water-soluble fraction increases to 0.3–0.5% due to free Cu(II) ions and their soluble complexes with inorganic anions or organic ligands. The content of the exchangeable fraction, which includes exchangeablysorbed Cu compounds bound to different soil components (clay minerals; Fe, Al, and Mn hydroxides; and organic matter), increases to 1%. The content of Cu in the acid-soluble fraction, which characterizes its binding to carbonates, is three- to fivefold higher than that in the exchangeable fraction. A peculiar feature of Calcic Chernozem is the presence of micellar carbonates with a large specific surface area, which increases their activity in interaction with metals. Thus, an increase in the mobility of the metal is observed under contamination, which is manifested in increased relative contents of water-soluble, exchangeable, and acid-soluble fractions (Figure 1).

The content of organic matter-bound Cu increases under contamination from 11 to 29% as compared to the uncontaminated sample (Figure 1). Similar changes in the composition of metal compounds were noted earlier for soils of technogenic landscapes (Minkina et al., 2014).

Along with organic matter and clay minerals, Al, Fe, and Mn oxides and hydroxides play a significant role in the adsorption of HMs in soils. The addition of Cu to the soil insignificantly increases the content of the metal in the Mn oxide-bound fraction compared to the uncontaminated sample. This is related to the special importance of the separation of this fraction by the Miller method for soils with high Mn contents. The content of Mn in the studied soil is 860 mg/kg (Mn clarke for soils is 850 mg/kg, Vinogradov, 1957).

The addition of Cu nitrates and oxides increases the content of the metal in the fractions bound to amorphous Fe oxides to 12 and 6%, respectively, while the content of Cu in the fractions bound to crystalline Fe decreases to 5 and 3%, respectively (Figure 1). This changes the distribution of Cu among the separated fractions compared to the original soil: silicate-bound (residual) fraction > organic matter-bound fraction > amorphous Fe-bound fraction > crystalline Fe-bound fraction >Mn oxide-bound fraction > acid-soluble fraction > exchangeable fraction ~ water-soluble fraction.

The age of soil contamination can be estimated from the presence of the fraction bound to amorphous Fe oxides (Vodyanitskii, 2010). The crystallization of Fe oxides proceeds for a sufficiently long time, and an abrupt increase in the content of metals in the amorphous Fe oxide indicates a recent contamination. The relative content of the fraction bound to amorphous Fe almost doubles at the addition of soluble copper nitrate, while the difference from the contaminated soil is insignificant, if any, at the addition of copper oxide (Figure 1).

During the incubation of soil with CuO, the increase in the share of Cu in the residual fraction to 74% (Figure 1) is related to the potential entry of Cu in the form of isomorphic impurities into silicates, as well as to the incomplete dissolution of exogenic metal compounds at the high level of their input into the soil (Minkina et al., 2010).So, the content of metal in the residual fraction at the addition of Cu oxide at 2000 mg/kg is higher than at the addition of the equivalent rate of Cu nitrate (Figure 1).

Experimental X-ray powder diffraction patterns for the original soil sample and the mineral phases of layered silicates phase (for example montmorillonite)and after modification with a saturated $Cu(NO_3)_2$ solution are shown in Figure 2.
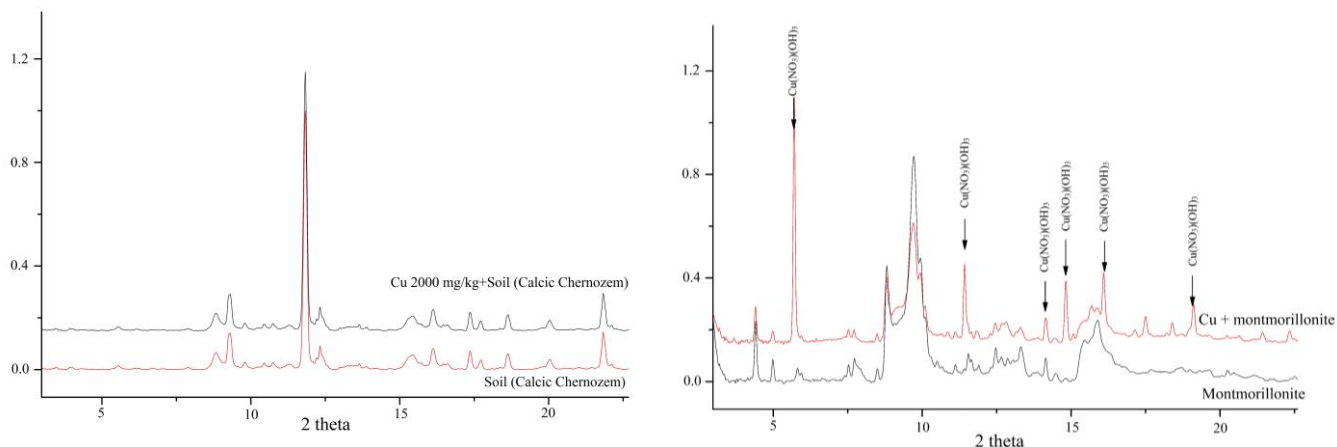

Figure 2. Comparative analysis of X-ray powder diffraction patterns for soil sample and layered silicate phase (for example montmorillonite) before and after modification with a saturated $Cu(NO_3)_2$ solution

The comparison of diffraction patterns for the soil sample and layered silicate phases (for example montmorillonite) before and after modification with a saturated $Cu(NO_3)_2$ solution (Figure 2) showed no appreciable changes in the diffraction pattern of the contaminated soil compared to the original samples. However, additional diffraction peaks corresponding to a new crystalline phase appeared in the diffraction patterns of layered phases saturated with Cu(II) ions.

A peculiar feature of layered silicate phases is the chemical and energetic heterogeneity of their surface characterized by the presence of structural defects and different functional groups, which can act as active centers during metal adsorption. These active centers on the surface of, e.g., montmorillonite can include exchangeable cations, surface hydroxyl groups, and oxygen atoms of the tetrahedral lattice. Some active centers occur on the lateral faces of minerals formed during the splitting of minerals.

The saturation of separate phases of layered silicates with a $Cu(NO_3)_2$ solution at a constant pH of 3.9 increases the share of acidic active centers, which affects the proportions of acid–base active centers on the surface of mineral phases (Ponizovskii and Mironenko, 2001). Hydrolysis processes, which shift the system equilibrium, also contribute. During the initial saturation period, Ca(II) cations are desorbed from the interlayer positions of layered silicates, especially smectites, into the contacting solution.

X-ray diffraction data showed that Cu^{2+} ions are sorbed from the saturated solution by active centers on the internal surface of the lattice of dioctahedralaluminosilicates, and surface hydroxyls at the octahedrally coordinated aluminum atom play the main role (Furnare et al., 2005; Strawn and Baker, 2009). X-ray diagnostics revealed that excess Cu(II) ions are removed from the system due to the formation and precipitation of coarsely crystalline $Cu(NO_3)(OH)_3$ (Figure 2). This fact agrees with the chemical fractionation data (Figure 1), which indicate an increase in the content of Cu in the silicate-bound residual fraction.

XANES data for the studied soil samples and mineral phases of layered minerals artificially contaminated with $Cu(NO_3)_2$ are shown in Figure 3.

Comparison of the first-derivative Cu K-edge XANES spectra for all samples with the spectrum of the $Cu(NO_3)_2$ standard showed sensitivity of the method for changes in the immediate surrounding of Cu(II) ions in these structures. The samples are characterized by the existence of peak A in the middle part of the spectrum (~899–8995 eV) due to the presence of Cu^{2+} ions. The absence of chemical shift of the main

absorption edge in contrast to the initial spectrum of the compound indicates that the charge of Cu^{2+} ion in the soil does not change.
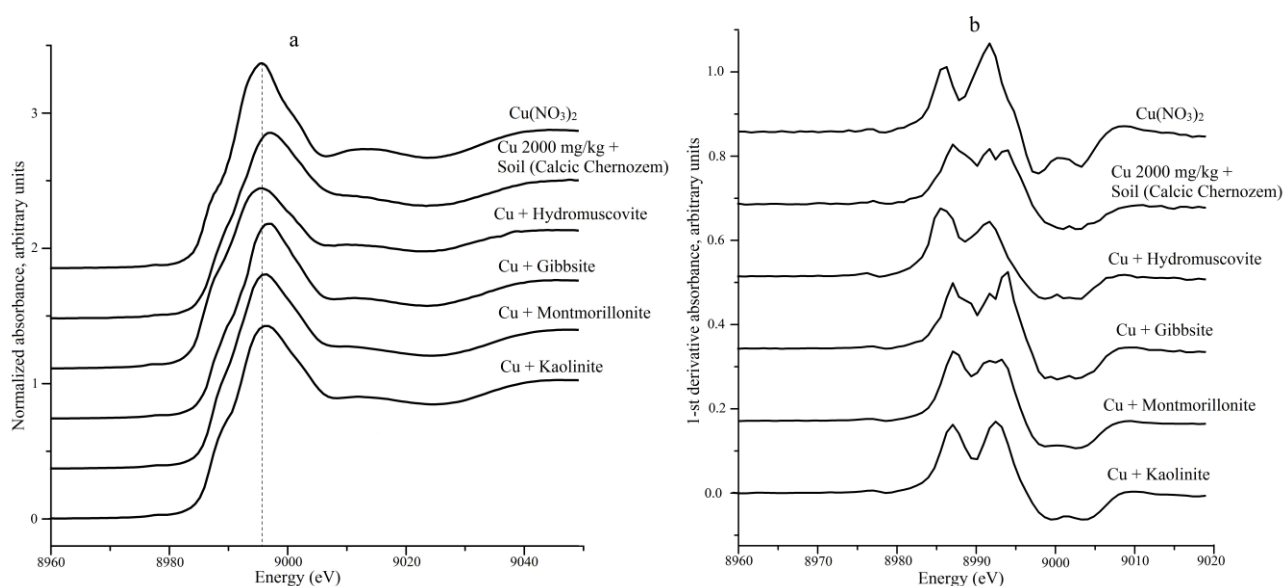

Figure 3. (a) Experimental Cu K-edge XANES spectra and (b) 1-st-derivative X-ray absorption spectra for soil, layered silicate phases, and $Cu(NO_3)_2$ standard

The spectral features of the central peak and low-amplitude lateral maximums of layered silicates, their shapes, and shifts against the original copper-containing compound indicate a shortening of interatomic distances between the adsorbed Cu^{2+} ions and the oxygen surrounding in accordance with the Natoly rule (Natoli, 1984). This agrees with data of X-ray diffraction analysis and earlier molecular dynamic simulation (Minkina et al., 2013).

Conclusion

Thus, contributions of different Cu forms to the distribution of the metal among soil components are shown. It is found that the contamination of soils with a soluble Cu(II) salt increases the bioavailability of the metal; the role of organic matter and Fe oxides in the fixation and retention of Cu also increases. During the incubation of soil with Cu monoxide, the content of the metal in the residual fraction increases, which is relatedto the potential entry of Cu in the form of isomorphic impurities into silicates, as well as to the incomplete dissolution of exogenic metal compounds at the high level of their input into the soil.

XANES data revealed the mechanism for the structural transformations of Cu(II) ions: they are sorbed from the saturated solution by active centers on the internal surface of the lattice of dioctahedralaluminosilicates, and surface hydroxyls at the octahedrally coordinated aluminum atom play the main role. X-ray diagnostics revealed a shortening of interatomic distances between the adsorbed Cu(II) ions and O atoms due to the displacement of some Al(III) ions in octahedral positions.

Acknowledgements

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