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1 Effects of Co doping on the structure and physicochemical properties of
2 hausmannite (Mn₃O₄) and its transformation during aging

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26 **Abstract:** Hausmannite is a common low-valence manganese oxide mineral with a
27 distorted spinel structure in surficial sediments. Although natural Mn oxides often
28 contain various transition metal (TM) impurities, few studies have addressed the
29 substitution mechanisms of TMs, such as cobalt (Co), with hausmannite and induced
30 changes in the mineral physicochemical properties. In this study, Co-doped
31 hausmannites with final Co/Mn molar ratios of 0.05 and 0.11 were synthesized and
32 characterized by wet chemical analysis, powder X-ray diffraction (XRD), Fourier
33 transformed infrared spectra (FTIR), high resolution transmission electron microscope
34 (HRTEM), X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine
35 structure spectroscopy (XAFS). Co-doped samples have larger crystallite sizes and
36 smaller specific surface areas than those of the hausmannite without Co. The Co cations
37 exist in a mixed-valence of +3 and +2. Powder XRD and acid dissolution experiments
38 indicate that Co incorporates into the mineral structures, and increases the mineral
39 structural stability. Co K-edge extended X-ray adsorption fine structure (EXAFS)
40 analysis demonstrates that Co likely substitutes for lattice Mn(III). After aging at room
41 temperature for three years, $14.1 \pm 1.9\%$ of pure hausmannite is transformed to
42 manganite while only $2.6 \pm 0.7\%$ of manganite appears in the aged Co-doped sample
43 with an initial Co/Mn molar ratio of 0.10. These results provide new insights into the
44 incorporation mechanisms of TMs into low valence Mn oxides, and the stability of
45 these minerals in natural environments.

46 **Keywords:** Mn oxide, hausmannite, transition metal, cobalt, transformation.

47

48

49 **1. Introduction**

50 Manganese (Mn) oxide minerals in various geological settings are often enriched
51 in various transition metals (TMs). Incorporation of TMs into Mn oxides can modify
52 the mineral substructure, physicochemical properties and reactivity towards various
53 pollutants (Song et al., 2020; Yin et al., 2012). Our previous studies on the effects of
54 TMs on the reactivity of hexagonal birnessite towards various pollutants convincingly
55 demonstrate that the reactivity of these TM-containing minerals, which are close to
56 natural analogs, can be much different from those of the pure one. For example,
57 incorporation of Ni into hexagonal birnessite greatly reduces the adsorption densities
58 of heavy metals, Pb^{2+} or Zn^{2+} , on the minerals by 79-85% (Yin et al., 2012). The
59 removal efficiencies of Cr^{3+} from water by Co- and Ni-containing birnessites are 28-
60 55% and 67-78%, respectively, that of the pure birnessite (Yin et al., 2020a).

61 Hausmannite is not only the fifth most common Mn oxide mineral in soils and
62 sediments, but is also found in hydrothermal and metamorphic deposits (Chartier et al.,
63 1999; Giovannelli et al., 2012; Jarosch, 1987). It has a tetragonally deformed spinel
64 structure, elongated along the *c* axis, with Mn^{2+} occupying the tetrahedral sites and
65 Jahn-Teller active Mn^{3+} in the octahedral sites (Bordeneuve et al., 2010; Jarosch, 1987;
66 Sukhdev et al., 2020). Hausmannite is usually not only the precursor or secondary
67 product of other Mn oxide phases (Barreto et al., 2020; Birkner and Navrotsky, 2012;
68 Birkner and Navrotsky, 2014; Feng et al., 2004), but also can have adsorption and redox
69 reactivity towards a variety of metal pollutants (Barreto et al., 2020; Johnson et al.,
70 2018; Shaughnessy et al., 2003; Song et al., 2020; Wilk et al., 2005).

71 Being the most widely distributed Mn oxide spinel, hausmannite is capable of
72 housing various substituents, including Co, Ni, Fe and Al (Antao et al., 2019; Baron et
73 al., 1998; Bordeneuve et al., 2010; Green et al., 2004; Lefkowitz and Elzinga, 2015;
74 Rajeesh Kumar et al., 2021; Song et al., 2020). Substitution of Fe^{3+} for Mn^{3+} into the
75 octahedral site in hausmannite decreases the Jahn-Teller distortion, increases the Curie
76 point, and decreases the spontaneous magnetization (Baron et al., 1998). Zn doping
77 changes the morphologies of the obtained hausmannite crystallites from nanorods for
78 the pure mineral to a mixture of nanorods and nanoparticles, and increases the energy

79 bandgap (Jha et al., 2012). Pb doping greatly reduces the Mn_3O_4 particle size and
80 increases the bandgap, dielectric constant, and AC conductivity (Şahin et al., 2020).
81 Doping with various TMs (Cr^{3+} , Co^{2+} , Ni^{2+} , and Cu^{2+}) greatly enhances the phase
82 stability during cycling and charge-transfer behaviors of hausmannite (Dong et al.,
83 2013). However, these studies mainly focus on the applications of TM-modified
84 hausmannites in materials sciences. It is recently reported that Ni substitution in
85 hausmannite causes noticeable changes in the mineral structure (e.g. lattice parameters),
86 and enhances mineral acid dissolution and oxidation reactivity towards As(III) at pH =
87 5 (Song et al., 2020). This indicates that structural impurities may modify the structure
88 and physicochemical properties of hausmannite and thus the adsorption and redox
89 reactivity towards pollutants. Unlike Ni, Co is highly redox-sensitive, and the influence
90 of Co incorporation on the reactivity and stability of hausmannite remains to be
91 determined.

92 Further, as a kind of metastable mineral, hausmannite can be converted into other
93 Mn oxides phases during aging. These processes can be affected by mineral properties,
94 such as chemical composition and particle sizes, and environmental conditions, e.g.,
95 moisture, temperature and O_2 (Birkner and Navrotsky, 2012; Birkner and Navrotsky,
96 2014; Kirillov et al., 2009; Rabiei et al., 2005). At 60% relative humidity at room
97 temperature, hausmannite can change its morphology and chemical identity to
98 manganite (Rabiei et al., 2005). Upon slow oxidation at room temperature for 1 year,
99 the hausmannite content in a mixture of hausmannite with manganite is decreased from
100 47% to 28% (Kirillov et al., 2009). Small crystallite size is reported to promote
101 hausmannite transformation (Birkner and Navrotsky, 2012; Birkner and Navrotsky,
102 2014). These previous studies mainly focus on the aging of pure hausmannite. However,
103 the effect of TM doping on the stability of hausmannite and its transformation during
104 aging remains largely unexplored.

105 The present work aims to investigate the effect of Co doping on the mineral
106 structure, physicochemical properties and stability during aging at room temperature.
107 Specifically, Co-doped hausmannite samples were synthesized at room temperature by
108 a coprecipitation method, and characterized by powder XRD, FTIR and HRTEM. The

109 valence and crystal chemistry of Mn and Co were investigated by XPS, Co K-edge
110 XAFS and acid dissolution experiments. These findings will help in understanding the
111 effects of TM doping on the structure, properties and stability of low valence Mn oxide
112 minerals in natural environments.

113

114 **2. Materials and methods**

115 **2.1 Preparation of Co-doped hausmannites**

116 Cobalt substituted hausmannite was prepared according to the method described
117 in Giovannelli (Giovannelli et al., 2012). In detail, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ was added to 200 mL
118 of 0.5 M MnSO_4 solution to obtain an initial Co/Mn molar ratio of 0, 0.05 and 0.10.
119 After the solution was uniformly mixed, 2 M NaOH solution was added dropwise to
120 keep the suspension pH above 10 for 6 h under stirring in air at room temperature. The
121 pH was recorded by a pH-meter. At the end of the reaction, the slurry was filtered,
122 rinsed with deionized water until the conductivity of filtrate was $< 20 \mu\text{s cm}^{-1}$ to
123 eliminate the salt excess, and dried at 40 °C for 3 days, and then ground and sieved (100
124 mesh). The prepared samples were designated as HM, CoH5, and CoH10
125 correspondingly.

126 Portions of the HM and CoH10 powders were stored in closed tubes at room
127 temperature (25 ± 5 °C) under air condition in the laboratory for three years, and the
128 humidity in laboratory around 50%. The corresponding samples were named as
129 agedHM and agedCoH10.

130 **2.2 Sample characterization**

131 The phase purity of prepared samples was analyzed using a Bruker D8 Advance
132 diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm). The diffractometer was operated
133 at a tube voltage of 40 kV and a tube current of 40 mA in the range of 2θ of 5-85 ° at a
134 step of 0.02 ° and an integration time of 1.2 s. Rietveld structure refinements were
135 performed using software TOPAS (version 4.2). The specific surface areas (SSA) were
136 measured by N_2 adsorption at liquid nitrogen temperature (77 K) with an Autosorb-1
137 standard physical adsorption analyzer (Quantachrome Autosorb-1, USA). The samples
138 (100 mg) were degassed under vacuum at 110 °C for 3 h before N_2 adsorption, and SSA

139 was calculated by employing the multi-point BET method. HRTEM analysis and
140 selected-area electron diffraction were employed to obtain mineral morphologies,
141 particle sizes, and phase lattice on a JEM-2100F (JEOL, Japan) at 200 keV. The samples
142 were prepared by adding 50 μL of 0.1 $\text{g}\cdot\text{L}^{-1}$ mineral suspension onto a 200-mesh
143 carbon-coated copper grid (Beijing Zhongjingkeyi Technology Co., Ltd.), and dried at
144 room temperature under air condition. FTIR analyses were performed on a Bruker
145 Equinox 55 model spectrophotometer using KBr pellets with a spectral range of 4000-
146 400 cm^{-1} . XPS of Mn 2p and Co 2p were measured on a VG Multilab 2000 X-ray
147 photoelectron spectrometer with a Mg $\text{K}\alpha$ X-ray source (1253.6 eV) using the large
148 area mode with a pass energy of 25 eV and an energy step size of 0.1 eV. Adventitious
149 C 1s binding energy was used to calibrate the energy and set to 284.8 eV. Data were
150 analyzed using Avantage software, and a Shirley background was used (Yin et al., 2011).
151 For Mn 2p fitting, the fit parameters were used from a previous study (Ilton et al., 2016).

152 The sample chemical composition was determined via atomic absorption
153 spectrometry (AAS, Varian AAS 240FS) after dissolving 0.1000 g solid in a mixture of
154 25 mL of 0.25 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution and 1 M H_2SO_4 solution. Triplicate analyses
155 were performed. Method blanks and matrix spikes were also analyzed along with
156 samples for quality assurance and quality controls, and the spiked recoveries of Mn^{2+}
157 were between 98 and 102% (mean recovery: $100 \pm 2\%$).

158 **2.3 Dissolution experiments**

159 The acid dissolution experiment was performed by adopting the method in our
160 previous study (Qin et al., 2017). Briefly, 0.10 g sample was added into 250 mL of 2 M
161 HCl solution while stirring at a constant rate with a magnetic stir at room temperature.
162 At predetermined time intervals, an aliquot of 5 mL suspension was taken out and
163 immediately filtered through 0.22 μm membrane (Shanghai Xingya purification
164 material factory). The concentration of Mn^{2+} and Co^{2+} in the filtrate were analyzed using
165 AAS. The metal (Me) dissolution ratio was calculated as $\chi_{\text{Me}} = \text{Me}(t)/\text{Me}(\text{total})$, where
166 Me (t) is the concentration of metal in solutions at time t, and Me(total) is the final metal
167 concentration after complete dissolution of the mineral.

168 **2.4 X-ray absorption fine structure (XAFS) spectroscopy**

169 The XAFS data were collected at room temperature on the 1W1B beamline at the
170 Beijing Synchrotron Radiation Facility (BSRF) (Yin et al., 2012). Cobalt K-edge XAFS
171 data were collected in fluorescence mode over the energy range of 7510 to 8305 eV.
172 Reduction and analysis of XAFS data were performed using Athena and Artemis from
173 the IFEFFIT software package (Ravel and Newville, 2006). Cobalt K-edge spectra were
174 background-subtracted using the following parameters: $E_0 = 7716$ eV, $R_{bkg} = 1.0$ Å
175 and $k\text{-weight} = 2$. Structural parameters (bond length (R), coordination number (CN),
176 and Debye-Waller factor (σ^2)) were obtained by fitting the k^3 -weighted EXAFS data to
177 the standard EXAFS equation (Kelly et al., 2008). Phase and amplitude functions were
178 calculated using FEFF7.0 (Rehr et al., 1992). The Co K-edge EXAFS data were fitted
179 in an R space of 1-4 Å over a k range of 3.1-12.0 Å⁻¹, using several single scattering
180 paths calculated by substituting Co for tetrahedral or octahedral Mn in the hausmannite
181 structure (ICSD 76088). An amplitude reduction factor (S_0^2) of 0.877 for Co was
182 adopted from our previous studies (Yin et al., 2014). In all fits, the number of
183 independent variables was much smaller than that of the independent data points
184 allowed. During Fourier transformation and EXAFS data fitting, a Hanning window
185 was used.

186

187 **3 Results**

188 **3.1 Powder XRD**

189 Three synthesized samples display similar XRD patterns (Fig. 1a), which coincide
190 well with the tetragonal hausmannite standard (ICDD 89-4837). The main characteristic
191 reflections at ~ 3.10 Å, ~ 2.77 Å, ~ 2.49 Å, ~ 1.58 Å, and ~ 1.54 Å can be indexed to (112),
192 (103), (211), (321), and (224), respectively (Giovannelli et al., 2012; Zhao et al., 2011).
193 With an increase in Co content, the peak positions of the ($hk0$) reflections do not change
194 but those of (hkl) reflections shift to higher angles, indicating a decrease of unit-cell
195 parameter c . Rietveld refinements of these samples were performed using the
196 hausmannite structure (ICSD 76088) as the starting model. Because of the similarity of
197 the Co and Mn X-ray scattering factors, the refinements were not able to provide
198 information about ordering of the Co cations over the tetrahedral and octahedral sites

199 or the Co valence. The refinements were thus carried out assuming all Mn, and the
200 results are listed in Fig. 1a and Table S1. From HM to CoH10, unit-cell parameter a is
201 essentially constant at 5.771-5.774 Å, while parameter c systematically decreases from
202 9.477 ± 0.002 Å to 9.370 ± 0.002 Å. The indicator of Jahn-Teller distortion of the
203 $[\text{Mn(III)O}_6]$ octahedron in hausmannite, $c/(1.414a)$, likewise decreases from $1.1613 \pm$
204 0.0003 for HM to 1.1479 ± 0.0004 for CoH10, indicating the reduction of Jahn-Teller
205 distortion after Co doping (Bordeneuve et al., 2010; Hirai et al., 2016; Kim et al., 2012).
206 In hausmannite, the $[\text{Mn(III)O}_6]$ octahedra are elongated along the $[001]$ direction
207 (Jarosch, 1987), therefore the decrease in c and the Jahn-Teller distortion indicator
208 clearly confirm the replacement of lattice Mn^{3+} by the smaller $\text{Co}^{2+/3+}$ and/or Mn^{4+}
209 (Bordeneuve et al., 2010; Hirai et al., 2016; Shannon, 1976; Song et al., 2020). The
210 coherent scattering domain (CSD) sizes determined by the refinements for HM, CoH5
211 and CoH10 are 59.1 ± 0.7 nm, 91.6 ± 1.1 nm and 74.9 ± 1.3 nm, respectively. This may
212 suggest that Co doping promotes the hausmannite crystal growth at the experimental
213 conditions.

214 The powder XRD analysis of three years aged HM (agedHM) and CoH10
215 (agedCoH10) is plotted in Fig. 1b. In addition to the main reflections of hausmannite
216 (ICSD 76088), there is an additional peak at 2θ of 26.18° in agedHM. This peak
217 coincides well with that of manganite (ICSD 84949). This peak also appears in
218 agedCoH10, but with much lower intensity than that in agedHM. This suggests that Co-
219 doped hausmannite sample undergoes slower oxidation at room temperature during
220 aging in the dry state than that of pure hausmannite. Quantitative phase analysis of these
221 aged samples were performed using the hausmannite (ICSD 76088) and manganite
222 structure (ICSD 84949). The results are depicted in Fig. 1b and Table S2. For agedHM,
223 the contents of hausmannite and manganite are $85.9 \pm 1.9\%$, and $14.1 \pm 1.9\%$,
224 respectively. For agedCoH10, the contents of hausmannite and manganite are $97.4 \pm$
225 0.7% and $2.6 \pm 0.7\%$, respectively.

226 3.2 Elemental analysis, specific surface areas and morphologies

227 With increasing Co content, the Mn content decreases from $70.92 \pm 0.01\%$ for HM
228 to $69.63 \pm 0.32\%$ and $65.93 \pm 1.16\%$ for CoH5 and CoH10, respectively. The final

229 Co/Mn molar ratios in these samples are approximately the same as those in the initial
230 reactants. The specific surface area (SSA) of HM is $12.4 \text{ m}^2 \cdot \text{g}^{-1}$, and decreases to 11.7
231 $\text{m}^2 \cdot \text{g}^{-1}$ and $11.8 \text{ m}^2 \cdot \text{g}^{-1}$ for CoH5 and CoH10, respectively.

232 Fresh HM crystals are composed of irregular cubic particles (Fig. 2a), which is
233 consistent with previous studies (Giovannelli et al., 2012; Hao et al., 2011; Zhang et al.,
234 2011). Co-doped hausmannite crystals are uniformly composed of cubic particles (Fig.
235 2b, c), which are also similar to Co-doped hausmannite samples in previous studies
236 (Dong et al., 2013). Statistical analysis of the particle sizes of these samples gives an
237 average size of $85 \pm 18 \text{ nm}$ of HM, $131 \pm 27 \text{ nm}$ of CoH5 and $103 \pm 28 \text{ nm}$ of CoH10
238 (Fig. S1). These physical sizes coincide well with the CSD sizes obtained by powder
239 XRD analysis. Both suggest that Co-doped samples have larger sizes than the pure one.
240 This may indicate that Co ions play a significant role in the growth and assembly of
241 hausmannite initial crystals, and a low amount of Co may favor the crystal growth of
242 hausmannite; but further increasing the Co content will cause structural defects in the
243 mineral structure and thus retard the crystal growth.

244 In order to confirm whether these Co-doped hausmannite samples are stable during
245 dry storage at room temperature, the HRTEM and SAED patterns of the samples
246 obtained after aging for 3 years, agedHM and agedCoH10, are also presented in Fig.
247 2d-i. There are plenty of lath-like crystals in agedHM, besides the cubic crystals (Fig.
248 2d). The SAED pattern of the cubic crystal (Fig. 2e) confirms that the cubes are pure
249 hausmannite single crystals. In the HRTEM image of the lath crystal (Fig. 2f), a lattice
250 distance of 0.339 nm is observed, matching well with that of manganite. The crystals
251 of agedCoH10 retain their cubic shapes for hausmannite (Fig. 2g), which is also
252 confirmed by HRTEM and SAED (Fig. 2h, i).

253 3.3 FTIR

254 The FTIR spectra of these freshly prepared Co-doped hausmannite samples have
255 four peaks located at 408 , 525 , 629 , and 3415 cm^{-1} (Fig. 3). These bands coincide well
256 with those of hausmannite (Kirillov et al., 2009). The 3415 cm^{-1} band is assigned to OH
257 vibrations of physisorbed water molecules, while the three other peaks from left to right
258 correspond to wagging, bending and stretching vibrations of $[\text{MnO}_6]$ and $[\text{MnO}_4]$ units

259 (Julien et al., 2004; Kirillov et al., 2009).

260 After three years aging in the dry state, the spectra of these hausmannites change.
261 Firstly, a peak at 1630 cm^{-1} appears (Fig. 3). As this peak corresponds to molecular H_2O
262 bending vibrations (Kim et al., 2002), the presence of this peak suggests there is a
263 quantity of physisorbed water on the mineral surfaces and/or in the structures. Secondly,
264 although the main peaks for hausmannite are preserved in the spectrum of agedHM, the
265 relative intensities of the peaks belonging to manganite, such as 440, 484, 597, 1085,
266 1116, 1152, 2075 and 2655 cm^{-1} have increased. This indicates a significant portion of
267 hausmannite is transformed into manganite during the aging (Kirillov et al., 2009;
268 Kohler et al., 1997). Additionally, careful inspection of the spectrum of agedCoH10
269 shows that, the original 525 cm^{-1} peak of fresh CoH10 is shifted to 508 cm^{-1} for
270 agedCoH10, and there are three small additional peaks at 1085, 1116 and 1152 cm^{-1} ,
271 indicating the presence of a minor amount of manganite (Fig. 3e-h). This agrees well
272 with the XRD analysis. Additionally, the bands for agedHM and agedCoH10 are weaker
273 and broader relative to the initial samples, owing to the coexistence of several Mn oxide
274 phases.

275 3.4 Mn 2p XPS spectra

276 Manganese 2p spectra of these samples are used to investigate the proportions of
277 various Mn species on the mineral surfaces. With Co content increasing, the peak
278 binding energy (BE) shifts to low BE side (Fig. 4a). For example, the Mn $2p_{3/2}$ BE is
279 decreased from 641.94 eV for HM to 641.01 eV for CoH10, indicating the decrease of
280 the Mn average oxidation state (AOS). Further quantitative fitting analysis of the
281 spectrum using multiplet parameters (Ilton et al., 2016) are conducted (Fig. 4b, c and
282 Table S3). The HM spectrum can be decomposed to 28% Mn^{2+} , 58% Mn^{3+} and 14%
283 Mn^{4+} . With the increase of the dopant level, the relative proportions of Mn^{3+} and Mn^{4+}
284 are decreased but that of Mn^{2+} is increased. The spectrum of CoH10 can be decomposed
285 to 39% Mn^{2+} , 54% Mn^{3+} and 7% Mn^{4+} . The calculated Mn AOSs are 2.86 ± 0.02 and
286 2.69 ± 0.02 for HM and CoH10, respectively.

287 3.5 Acid dissolution experiments

288 Fig. 5 shows the fraction of dissolved Co or Mn (χ_{Co} or χ_{Mn}) vs. time, and $\chi_{\text{Co}} - \chi_{\text{Mn}}$

289 curves of the Co-doped samples in 2 M HCl solution at room temperature. For both
290 samples, the χ_{Co} or χ_{Mn} vs. time curves show a fast initial rate, followed by a gradual
291 decrease until the dissolution is complete, and the dissolution of Co is slightly quicker
292 than that of Mn. To obtain the Mn and Co dissolution rate constant (K), Kabai equation,
293 $\chi_{\text{Metal}} = 1 - \exp(-(\text{K} \cdot t)^a)$, is employed to model the dissolution curves (Alvarez et al., 2007;
294 Liu et al., 2019). With Co content increasing, the Mn dissolution rate constant (K_{Mn}) is
295 decreased from $0.2823 \pm 0.0301 \text{ min}^{-1}$ for CoH5 to $0.2070 \pm 0.0175 \text{ min}^{-1}$ for CoH10.
296 These results indicate that doping Co makes the mineral structure more stable and more
297 resistant to proton attack. This may be related to the higher bond dissociation energy
298 (BDE) of Co-O ($397 \pm 9 \text{ kJ} \cdot \text{mol}^{-1}$) than that of Mn-O ($362 \pm 25 \text{ kJ} \cdot \text{mol}^{-1}$) (Lide and
299 “Mickey” Haynes, 2010). According to the BDE, it is expected that Mn cations will be
300 slightly easier to be released out of the lattice than Co cations. In contrast, the
301 dissolution-rate constant of Co is much higher than that of Mn, and increases with
302 increasing the Co content in the sample. The Co dissolution rates (K_{Co}) in these samples
303 are $0.6516 \pm 0.0724 \text{ min}^{-1}$ for CoH5 and $0.8743 \pm 0.0804 \text{ min}^{-1}$ for CoH10, respectively.
304 This may suggest that Co may not occupy completely the same lattice sites as Mn. But
305 it should also be noteworthy that, the mineral dissolution in HCl solution is a much
306 complex process, which involves protonation, complexation, and reduction induced
307 dissolutions by Cl^- (Cornell and Schwertmann, 2003). It can be affected by many other
308 factors such as crystal sizes, coexisted cations, H^+ concentration and so on. Particles
309 with smaller crystal sizes are dissolved faster than those with large crystal sizes
310 (Alvarez et al., 2007; Cornell and Schwertmann, 2003). The obtained α values for χ_{Co} -
311 t or χ_{Mn} - t for CoH5 and CoH10 are also the same, confirming the purity of these
312 minerals. Further, the χ_{Co} - χ_{Mn} curves are a little convex with respect to the $Y=X$ line.
313 This suggests Co incorporates into the mineral structures but is slightly preferentially
314 enriched in the rims of the crystals (Qin et al., 2017; Yin et al., 2014).

315 **3.6 Co K-edge XAFS analysis**

316 **3.6.1 X-ray adsorption near edge structure (XANES)**

317 The Co K-edge XANES profiles of the two Co-doped hausmannite samples, CoH5

318 and CoH10, are distinct from but intermediate between those of the reference
319 compounds CoSO₄ and CoOOH (Fig. 4d), suggesting a mixed-valence of Co in these
320 samples. Linear combination fitting analysis further quantitatively confirms this (Fig.
321 4d and Table S4). The results show that CoH5 and CoH10 both contain 66-67% Co³⁺
322 and 33-34% Co²⁺. Previous studies reported that Co exists as only Co²⁺ in Co-
323 containing hausmannite (Mn_{3-x}Co_xO₄, 0 < x < 1) samples synthesized under mild
324 alkaline conditions and at high temperature (Bordeneuve et al., 2010; Dong et al., 2013;
325 Hirai et al., 2016). In contrast, the samples used here were synthesized using a
326 coprecipitation method at room temperature and at pH > 10.

327 3.6.2 EXAFS

328 The k³-weighted Co K-edge EXAFS and the corresponding Fourier transformed
329 spectrum (FT) of typical Co-doped sample, CoH10, are different from those of CoOOH
330 and CoSO₄ references (Yin et al., 2015), indicating neither CoOOH precipitate nor free
331 Co²⁺ exists (Fig. 6a,b). As both powder XRD analysis and acid dissolution confirm the
332 incorporation of Co into the mineral structures, Co can exist in either an octahedral or
333 a tetrahedral coordination or both. The oscillations of CoH5 and CoH10 are essentially
334 the same (Fig. 6c,d), indicating that Co ions in the two samples have similar
335 coordination environments. The corresponding FTs show two strong backscattering
336 neighbors at R + ΔR ~ 1.5 Å and ~ 2.9 Å. The former corresponds to the first Co-O pair,
337 and the later can be deconvoluted into several Co-Me (Me = Mn and Co) pairs
338 (Bordeneuve et al., 2010).

339 To obtain more detailed information about the local structures of Co in the Co-
340 doped hausmannite samples, the Co K-edge EXAFS spectra of CoH5 and CoH10 are
341 analyzed with shell-by-shell fits (Fig. 6c, d and Table 1). The results indicate an average
342 Co-O distance of 1.97 ± 0.02 Å, which is slightly longer than those (1.90-1.91 Å)
343 previously reported for octahedral Co³⁺ (Manceau et al., 1997; Yin et al., 2013; Yin et
344 al., 2015), but much shorter than for octahedral Co²⁺ (2.09 Å) (Manceau et al., 1997).
345 This further suggests the coexistence of Co³⁺ and Co²⁺ in the hausmannites. Although
346 cations in tetrahedral coordination, such as Zn²⁺, typically form shorter distances with
347 the first coordination O (Kwon et al., 2009), the case for Co is complex. It was reported

348 that in YBaCo_4O_7 , the average tetrahedral Co-O distance ranges from 1.90-1.92 Å
349 (Valldor and Andersson, 2002). Thus, it is difficult to distinguish octahedral from
350 tetrahedral Co based on Co-O distances alone. The fits also indicate longer Co-Me
351 (Me=Co, Mn) correlations at radial distances of 2.80-2.82, 3.01-3.02, 3.36-3.38 and
352 3.77-3.78 Å (Table 1). These values correspond to the distances between edge-sharing
353 octahedra in the a - and c -direction, and corner-sharing octahedron-tetrahedron pairs in
354 the a - and c -direction, respectively, matching well with those for Co located in the
355 octahedron sites (Table S1). Further, when comparing to the corresponding average Me-
356 Me distances obtained by Rietveld structure refinements (Table S1), these Co-Me
357 distances are shorter, owing to the smaller radius of Co(III) (Shannon, 1976).

358 EXAFS fittings assuming that all the Co cations occupy the tetrahedral sites are
359 also conducted. An average Co-O distance of 1.96 ± 0.01 Å is derived, which is almost
360 the same as that determined assuming all octahedral Co. An attempt to fit the $R + \Delta R \sim$
361 2.9 Å peak by combining four paths: two paths for octahedron-tetrahedron corner-
362 sharing pairs in the a - and c -axis, a path for the nearest tetrahedron-tetrahedron pairs
363 and a Co-O path corresponding to that between the center Mn in a tetrahedron and its
364 second shell O belonging to the corner-sharing octahedron, does not yield a reasonable
365 fit. This suggests that the vast majority of Co cations occupy the octahedral sites in Co-
366 doped hausmannites (Song et al., 2020).

367

368 4. Discussion

369 4.1 Co valence and crystal chemistry in Co-doped hausmannite

370 Cobalt K-edge XANES analysis showed that Co^{2+} and Co^{3+} coexist in the Co-
371 doped hausmannites. Interestingly, the $\text{Co}^{3+}/\text{Co}^{2+}$ ratios keep almost the same, ~ 2 , for
372 CoH5 and CoH10. Owing to the high redox potential of $\text{Co}^{3+}/\text{Co}^{2+}$ pair ($E^0 = 1.92$ V)
373 (Lide and “Mickey” Haynes, 2010), O_2 and high valence Mn in the mineral, and surface
374 catalytic oxidation may account for the Co^{2+} oxidation. The oxidation of Co^{2+} is highly
375 related to the solution conditions, e.g. pH and temperature. Generally, a high
376 concentration of OH^- and high temperature favors the oxidation (Alvarez et al., 2008;
377 Pozas et al., 2004; Yin et al., 2020b). The coexistence of Co^{2+} and Co^{3+} in the doped

378 hausmannite samples is similar to that observed in Co-doped goethite samples in our
379 previous study (Yin et al., 2020a), both owing to the low alkalinity and low temperature
380 used. However, in the Co-doped goethite series, the $\text{Co}^{3+}/\text{Co}^{2+}$ ratio increases with
381 increasing initial Co concentration. This is ascribed to the catalytic oxidation of Co^{2+}
382 on the mineral precursor (e.g. ferrihydrite) surfaces driven by the electric potential
383 energy, which is dependent on the redox cation concentration (Boland et al., 2013; Lan
384 et al., 2017; Yin et al., 2020a). The constant $\text{Co}^{3+}/\text{Co}^{2+}$ ratio here may possibly be
385 explained by the absence of surface catalytic oxidation behaviors on hausmannite
386 surfaces, because hausmannite is an insulator (Bordeneuve et al., 2010).

387 Powder XRD, acid dissolution experiments and Co K-edge EXAFS analysis
388 demonstrate that the Co cations are incorporated into the mineral structures. In
389 hausmannite, Mn^{2+} occupies the tetrahedral site while Mn^{3+} occupies the octahedral
390 sites. However, when exotic cations are incorporated into the structure, the crystal
391 chemistry of the exotic cations are complex. Structure analysis of cobalt manganese
392 oxide spinel ($\text{Mn}_{3-x}\text{Co}_x\text{O}_4$) ($0 \leq x \leq 3$) synthesized at 800 °C demonstrates that the
393 tetrahedral Mn is first preferentially substituted by Co for $x < 1$, and then the octahedral
394 Mn is replaced by Co with increasing x value. It also shows that Mn^{2+} and/or Co^{2+} fill
395 the tetrahedral sites while Mn^{3+} , Co^{2+} , low-spin state Co^{3+} and Mn^{4+} occupy the
396 octahedral site (Bordeneuve et al., 2010). For a series of $\text{Mn}_{3-x}\text{Co}_x\text{O}_4$ samples ($0 \leq x \leq$
397 1.5) synthesized at ~ 20 °C by coprecipitation of the mixtures of Mn^{2+} and Co^{2+} solution
398 using $\text{NH}_3 \cdot \text{H}_2\text{O}$, the Mn(III)O_6 distortion indicator, $c/\sqrt{2a}$, almost overlaps with those
399 for the samples from the previous study when $x < 1$, and Co cations in these samples
400 was thought to solely occupy the tetrahedral sites (Hirai et al., 2016). Comparison of
401 the $c/\sqrt{2a}$ of the Co-doped hausmannite samples in the present study with those from
402 previous studies indicates that there is a good linear relationship between Co content
403 and $c/\sqrt{2a}$ for all these samples when $x < 1$, but the dependence of $c/\sqrt{2a}$ to the sample
404 Co content varies much. The $c/\sqrt{2a}$ of our samples decreases much faster with
405 increasing Co content than that in literatures, with a slope ~ 2 times that of the later
406 (Fig. 7). This may indicate that the crystal chemistry of Co in our samples is not the
407 same as that in the previous studies, owing to the fact that the mineral preparation

408 method will affect the detailed crystal chemistry of Co (Zhao et al., 2017).

409 Further, there is a debate in the spin state of the cations in the hausmannite
410 structure. Some literatures reported that in the distorted spinel structure of hausmannite,
411 Mn^{2+} is in the low-spin state (LS) while Mn^{3+} is in the high-spin state (HS) (Bordeneuve
412 et al., 2010; Jarosch, 1987; Nogués and Poix, 1974). However, other studies adopted
413 that Mn^{3+} in hausmannite octahedral sites has a low-spin state while Mn^{2+} in tetrahedral
414 sites has a high-spin state (Boucher et al., 1971; Xu et al., 2005). According to
415 molecular orbital calculations, if the MnO_6^{9-} cluster has smaller exchange splitting of
416 the $2t_{2g}$ orbital and larger crystal field splitting, a transition of Mn(III) from HS to LS
417 can occur, in company with a decrease of Mn-O distance from 2.04 to 1.88 Å (Sherman,
418 1984). The average Mn-O distances in $[Mn(III)O_6]$ in our Co-doped hausmannites are
419 2.05-2.06 Å (Table S1). This probably suggests that Mn(III) in our hausmannites are
420 probably HS. In the normal spinel structure of Co_3O_4 , HS Co^{2+} occupies the tetrahedral
421 sites while LS Co^{3+} occupies the octahedral sites (Spencer and Schroerer, 1974). In order
422 to elucidate the possible distributions of various cations in these Co-doped hausmannite
423 samples, the basic physicochemical properties of these cations are compared (Table 2).

424 After Co doping, the proportions of Mn^{3+} and Mn^{4+} are decreased while that of
425 Mn^{2+} is increased with increasing dopant content. It is generally assumed that Co^{3+} in
426 octahedral sites exists mostly in the LS state (Burns, 1993; McKenzie, 1970; Yin et al.,
427 2013). The CFSE of LS Co^{3+} ($534.2 \text{ kJ}\cdot\text{mol}^{-1}$) is ~ 2.5 times larger than that of Mn^{3+} in
428 the hausmannite structure, and therefore, it is favorable for Co^{3+} to replace Mn^{3+} . This
429 is the same for LS Co^{2+} . The CFSE of octahedrally coordinated LS Co^{2+} ($198.2 \text{ kJ}\cdot\text{mol}^{-1}$)
430 is larger than that of HS Mn^{3+} in hausmannite, favoring the substitution of Mn^{3+} by
431 Co^{2+} . This is supported by the Co K-edge EXAFS analysis. Further, as the radius of LS
432 Co^{3+} in octahedral coordination is 12.7% smaller than that of HS Mn^{3+} , this substitution
433 also accounts for the decrease of unit-cell parameter c and the suppression of the Jahn-
434 Teller distortion. Further, the smaller CFSE of tetrahedral HS Co(II) ($58.7 \text{ kJ}\cdot\text{mol}^{-1}$)
435 than that of LS Mn(II) ($79.6 \text{ kJ}\cdot\text{mol}^{-1}$) in tetrahedron excludes the substitution of Co(II)
436 for tetrahedral Mn(II). Consequently, it is assumed that in the Co-doped hausmannite
437 samples low-spin Co^{2+} and Co^{3+} occupy the octahedral sites.

438 4.2 Hausmannite transformation during aging

439 After aging the pure hausmannite (HM) and Co-doped hausmannite (CoH10) in
440 dry state for three years, $14.1 \pm 1.9\%$ of manganite appears in agedHM while $2.6 \pm 0.7\%$
441 of manganite is observed in agedCoH10. This clearly suggests the transformation of
442 hausmannite to manganite. It is proposed that the transformation of hausmannite to
443 manganite involves O_2 and H_2O according to the following equation (eq. 1):



444 During hausmannite aging in dry state, Mn(II) on the mineral surfaces are
445 gradually oxidized by O_2 to form $-Mn=O$ groups. Then these groups react with
446 physisorbed H_2O , leading to the formation of $-Mn=(OH)_2$ groups. Finally $-Mn=(OH)_2$
447 groups are transformed to MnOOH, which is thought to be the rate-determining step
448 (Kirillov et al., 2009).

449 This transformation processes can be affected by many factors. In the present study,
450 the O_2 and H_2O concentrations are limited during hausmannite aging, which is stored
451 in a closed tube. Thus the transformation rate here is much lower than those in air
452 (Kirillov et al., 2009) and in high relative humidity(Rabiei et al., 2005). However, the
453 transformation rate of CoH10 is much lower than that of HM at same conditions. This
454 may be related to the substitution-induced changes in mineral physicochemical
455 properties, such as chemical composition, particle size and stability of the host mineral.
456 Although Co-doped hausmannite samples here show the same cubic morphology as
457 that of pure hausmannite, statistical analyses of TEM determined particle sizes and the
458 CSDs obtained by XRD show that the Co-doped crystals are larger than those of HM.
459 The increase in crystal sizes of CoH5 and CoH10 may make them more stable than HM
460 (Birkner and Navrotsky, 2014; Gillot et al., 2001), since smaller crystallite size is
461 reported to promote phase transformation (Birkner and Navrotsky, 2012; Birkner and
462 Navrotsky, 2014). Additionally, doping Co decreases the Mn^{3+} content, and suppresses
463 the Jahn-Teller distortion to make the mineral structure more stable than pure one. The
464 decrease of Mn^{3+} may also favor the formation of hausmannite rather than MnOOH
465 phase (Jha et al., 2012). Our results clearly show that, exotic cation substitution have
466 great impact on the transformation of hausmannite. Conclusively, the enrichment of

467 various TMs in hausmannite may be an important reason for the stability of these
468 minerals in natural environments.

469

470 **5. Conclusions and environmental implications**

471 Natural hausmannite analogs, including Co-substituted hausmannites with Co/Mn
472 molar ratios of 0.05 and 0.11 were synthesized at ambient conditions. Cobalt ions
473 existed as Co^{3+} and Co^{2+} , substituting for Mn^{3+} in the octahedral sites, which resulted
474 in suppression of the Jahn-Teller distortion and a commensurate decrease in the unit-
475 cell parameter c . These Co-doped hausmannite samples had decreased Mn AOS and
476 increased crystal sizes than HM. Acid dissolution experiments confirmed that Co
477 incorporated into the mineral structures, and made the mineral more stable. Cobalt K-
478 edge EXAFS analysis demonstrated that dopants occupied the octahedral sites in the
479 hausmannite structure. Cobalt doping greatly improved the hausmannite stability
480 during dry aging at room temperature. After three years of aging in a dry state, $14.1 \pm$
481 1.9% of hausmannite in HM was transformed to manganite, while only $2.6 \pm 0.7\%$ of
482 hausmannite in CoH10 was transformed to manganite.

483 Based on the excellent adsorption, reducing and oxidizing reactivity towards a
484 variety of metal pollutants (Antao et al., 2019; Baron et al., 1998; Bordeneuve et al.,
485 2010; Green et al., 2004; Lefkowitz and Elzinga, 2015; Song et al., 2020), hausmannite
486 may play an important role in mediating the mobility and fate of metal nutrients and
487 contaminants in terrestrial environments. The substitution of TM for lattice Mn in the
488 hausmannite structure may greatly modify the mineral physicochemical properties and
489 thus their reactivity. Carefully and accurately investigation of the reactivity of these
490 doped minerals, which are close to their natural analogues, with nutrients and pollutants,
491 may help us understand and predict the geochemical behaviors of elements of interest
492 in natural settings and also benefit us from the design and application of environmental-
493 friendly Mn oxide materials in pollutant control and remediation.

494

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650

651 **Table 1.** Co K-edge EXAFS structural parameters obtained from the fit of Co-doped
 652 hausmannites.

Octahedron	CoH5	CoH10
Co-O		
CN ^a	6	6
R (Å) ^a	1.968	1.970(12)
σ^2 (Å ²) ^a	0.0067(12)	0.0072
Co-Mn(Co) _{OES_x} ^b		
CN	2	2
R (Å)	2.821(65)	2.798(43)
σ^2 (Å ²)	0.0110(63)	0.0113(35)
Co-Mn(Co) _{OES_z} ^b		
CN	4	4
R (Å)	3.023(44)	3.005(29)
σ^2 (Å ²)	0.0110(63)	0.0113(35)
Co-Mn(Co) _{OTCS_x} ^b		
CN	4	4
R (Å)	3.360	3.383(19)
σ^2 (Å ²)	0.0068(30)	0.0055(11)
Co-Mn(Co) _{OTCS_z/TT} ^b		
CN	2	2
R (Å)	3.779(24)	3.771(19)
σ^2 (Å ²)	0.0011(17)	0.0032(17)
E ₀ (eV)	-3.4(33)	-1.9(21)
Chi Sq.	126.39	91.27
R factor	0.0617	0.0233

653 Notes: ^aCN = coordination number; R = interatomic distance; σ^2 = Debye–Waller factor;
 654 E₀ = energy shift; Chi Sq. = chi-squared statistic.

655 ^bOES_x and OES_z refer to edge-sharing octahedra in the x- and z-axis; OTCS_x and
 656 OTCS_z refer to octahedron-tetrahedron corner-sharing pairs in the x- and z-axis; TT
 657 refers to the nearest tetrahedron-tetrahedron pairs.

658

659 **Table 2.** Electron structure, octahedral coordination radius (CR), electronegativity (χ),
660 ionization potential (η), crystal field stabilization energy (CFSE), pairing energy (P)
661 and bond dissociation energy (BDE) of Mn and Co.

Cation		Electronic structure	Configuration	CR (Å) ^a	χ^b	η^c (eV)	Δ^d (kJ/mol)	CFSE ^d (kJ/mol)	P ^e (kJ/mol)	BDE ^c (kJ/mol)
Mn	II	3d ⁵	4(LS)	(e) ⁴ (t ₂) ¹	—	—	39.8	79.6	285.0	362 ± 25
			4(HS)	(e) ² (t ₂) ³	0.80	1.4934		0		
			6(LS)	(t _{2g}) ⁵	0.81	1.4903	89.8	179.6		
			6(HS)	(t _{2g}) ³ (e _g) ²	0.97	1.4407		0		
	III	3d ⁴	4(LS)	(e) ⁴	—	—	111.6	290.2	301.6	
			4(HS)	(e) ² (t ₂) ²	—	—		67.0		
			6(LS)	(t _{2g}) ⁴	0.72	1.7052	251.3	402.1		
			6(HS)	(t _{2g}) ³ (e _g) ¹	0.785	1.6753		150.8		
Co	II	3d ⁷	4(LS)	(e) ⁴ (t ₂) ³	—	—	48.9	58.7	250	
			4(HS)	(e) ⁴ (t ₂) ³	0.72	1.5882		58.7		
			6(LS)	(t _{2g}) ⁶ (e _g) ¹	0.79	1.5665	110.1	198.2		
			6(HS)	(t _{2g}) ⁵ (e _g) ²	0.885	1.5371		88.1		
	III	3d ⁶	6(LS)	(t _{2g}) ⁶	0.685	1.7913	248.4	534.2	282.6	
			6(HS)	(t _{2g}) ⁴ (e _g) ²	0.75	1.7614		89.0		

662 ^a Data adopted from Shannon (1976). ^b Data calculated according to Portier et al. (1994).

663 ^c Data from Lide and “Mickey” Haynes. (2010).

664 ^d Data from Burns (1993) and Huheey et al. (1993). These data were calculated by neglecting the electron
665 pairing energies and electron-electron effects for simplification.

666 ^e Data from Huheey et al. (1993). These values are for the free ions and may be 15-30% smaller when
667 cations are chemically coordinated because of the nephelauxetic effects.

668

669 **Figure Captions**

670 **Fig. 1** (a) Powder XRD patterns of HM and Co-doped hausmannite samples, overlaid
671 with the best Rietveld structure refinement results based on a hausmannite model (ICSD
672 76088). (b) Powder XRD patterns of three years aged Co-doped samples, agedHM and
673 agedCoH10, overlaid with the best calculated patterns by quantitative phase analysis
674 using a hausmannite model (ICDD 76088) and manganite model (ICSD 84949). Blue
675 lines are experimental data (Y_{obs}), red lines are calculated patterns (Y_{calc}), and the light
676 gray lines are the difference patterns (Diff)). The reflections of hausmannite are not
677 labeled while the main peak for manganite (γ -MnOOH) is indicated by dash line. (c)
678 Crystal diagram of hausmannite (ICSD 76088).

679 **Fig. 2** Typical TEM images of freshly prepared Co-doped hausmannite samples (a, HM;
680 b, CoH5; c, CoH10), and 3 years aged samples of (d) agedHM and (g) agedCoH10. (e)
681 and (i) show the SAED patterns of the areas in the blue rectangles in (d) and (g),
682 respectively, while (f) and (h) are typical HRTEM images for the area in the blue circle
683 in the inset at right down of panel (f) and the blue rectangle in panel (g) correspondingly.

684 **Fig. 3** FTIR spectra of freshly prepared and 3 years aged Co-doped hausmannite
685 samples and a synthesized manganite standard.

686 **Fig. 4** Mn 2p spectra of HM and CoH10 (a), and the corresponding Mn 2p_{3/2} spectra (b,
687 c) with the best fit overlaid (The black open circles represent experimental data, red
688 lines are the best fit to the data, peaks corresponding to Mn²⁺, Mn³⁺ and Mn⁴⁺ are shown
689 as green dot, dash and solid lines respectively, and the gray solid lines at the bottom are
690 the difference patterns). (d) Linear combination fitting (red dashed lines) of Co K-edge
691 XANES spectra of CoH5 and CoH10, using CoSO₄ and CoOOH (Yin, 2015 #50) as
692 references.

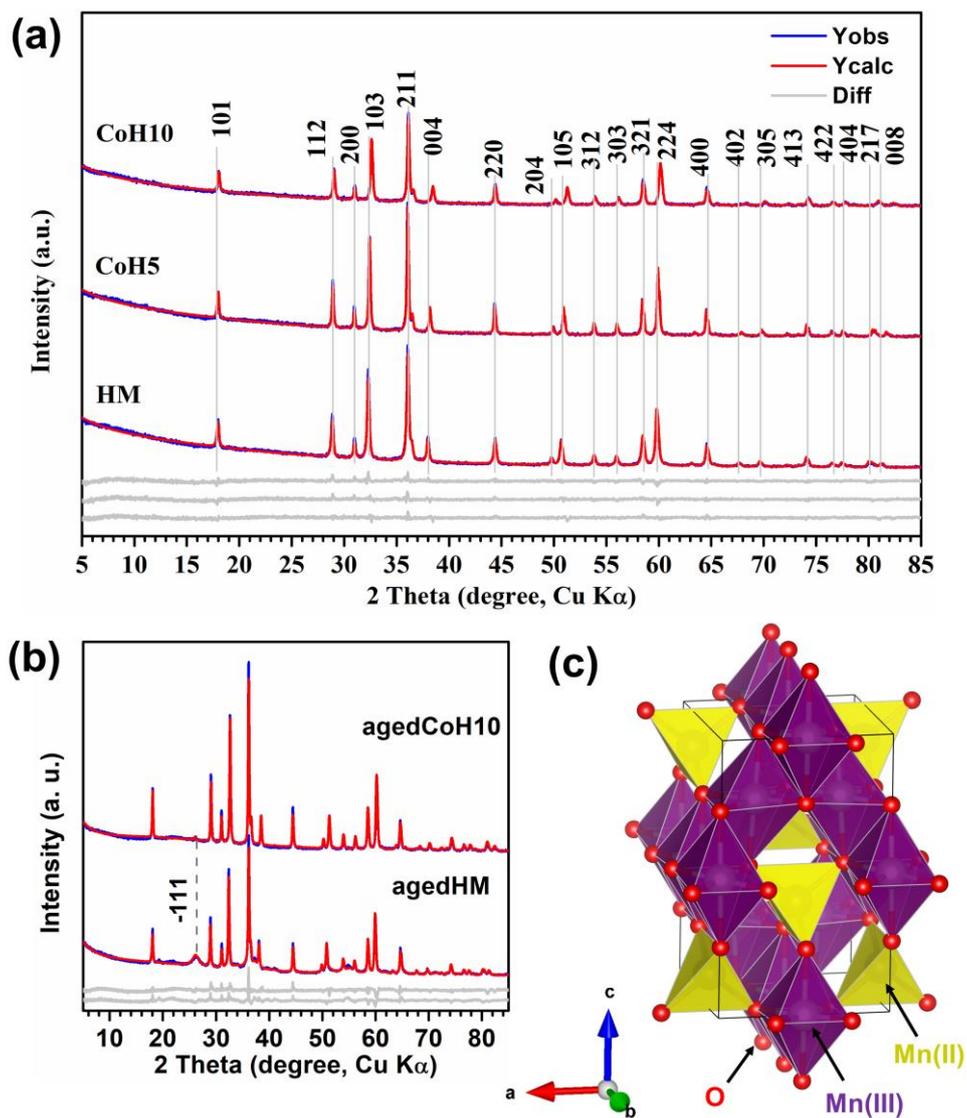
693 **Fig. 5** (a) Mineral dissolution kinetic curves expressed as %Co dissolved (χ_{Co}) or %Mn
694 dissolved (χ_{Mn}) in 2 M HCl solution at 25 °C and (b) the corresponding χ_{Co} versus χ_{Mn}
695 curves of these Co-doped hausmannite samples. In panel a, the inset is the detailed
696 figure in the first 12 h of the dissolution reactions, the solid lines are the best fit of the
697 whole dissolution curve with Kabai equation, $\chi_{Co(Mn)} = 1 - \exp(-(kt)^\alpha)$, in which k and
698 α are constants representing the dissolution rate constant and the characteristics of the

699 mineral structure, and the corresponding fitting parameters are listed in the table
700 inserted in the panel. In panel b, the red solid line is the 1:1 line.

701 **Fig. 6** Comparison of k^3 -weighted Co K-edge EXAFS (a) and the corresponding
702 Fourier transformed (FTs) spectra (b) of CoH10 and that of synthesized CoSO₄ and
703 CoOOH from our previous study (Yin et al., 2015). In panel b, the magnitudes of first
704 Co-O peaks were normalized. The Co K-edge EXAFS (c) and the corresponding
705 Fourier transformed (FTs) spectra (d) of CoH5 and CoH10, overlaid with the best fitting
706 by assuming that all the Co cations occupy the octahedral sites. Blue lines are
707 experimental data and dashed red lines are the best fits.

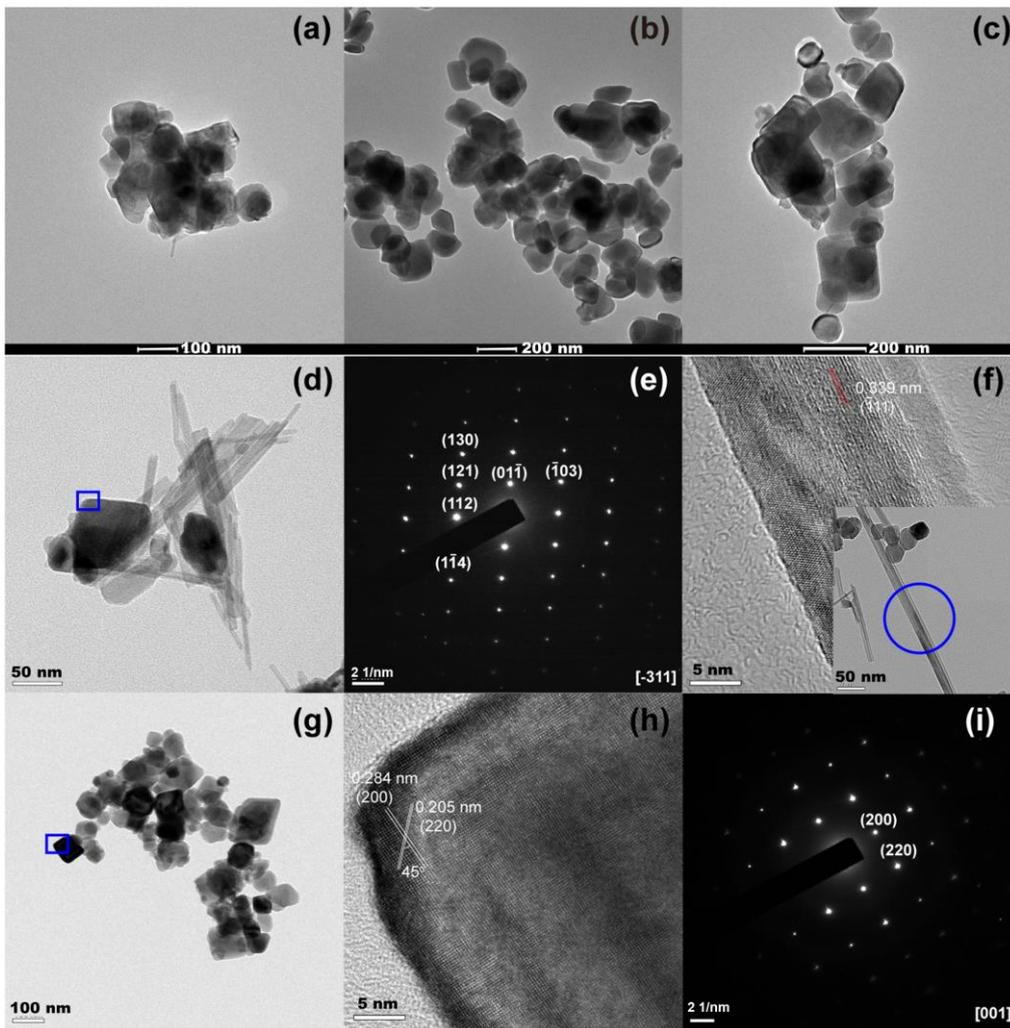
708 **Fig. 7** Comparison of the $c/\sqrt{2}a$ of the Co-doped hausmannite samples in the present
709 study with those of the Mn_{3-x}Co_xO₄ nanoparticles from previous studies (Bordeneuve
710 et al., 2010; Hirai et al., 2016; Rajeesh Kumar et al., 2021). The solid lines represent
711 the linear fitting of these data with $x < 1$.

712



713

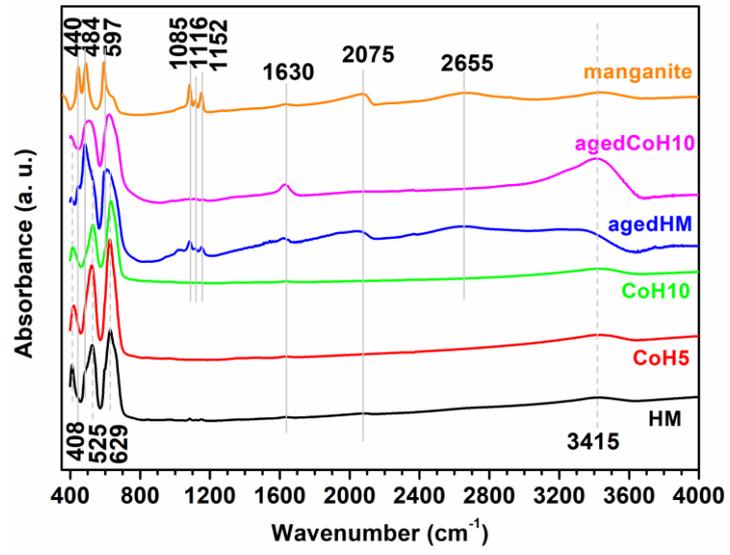
714 Fig. 1



715

716 **Fig. 2**

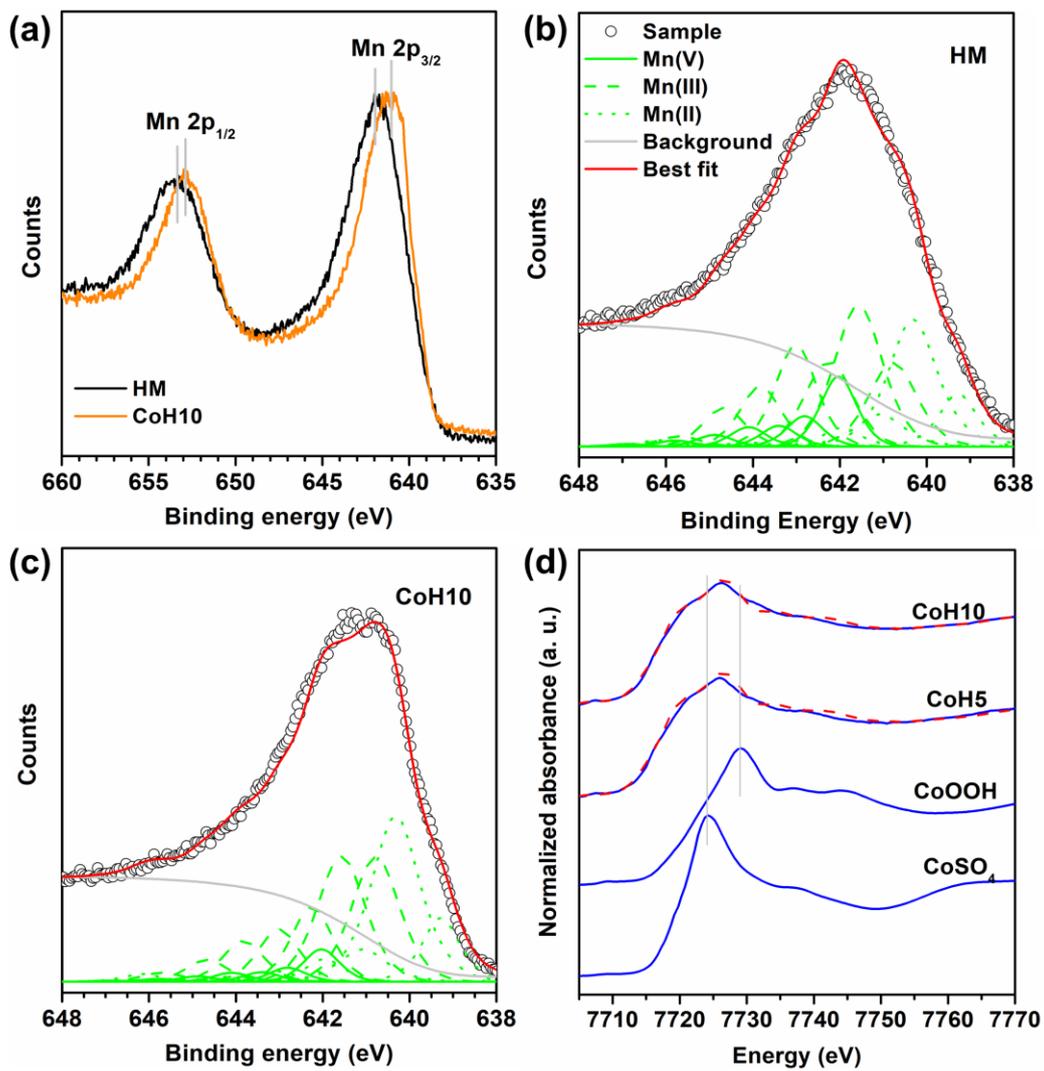
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719 **Fig. 3**

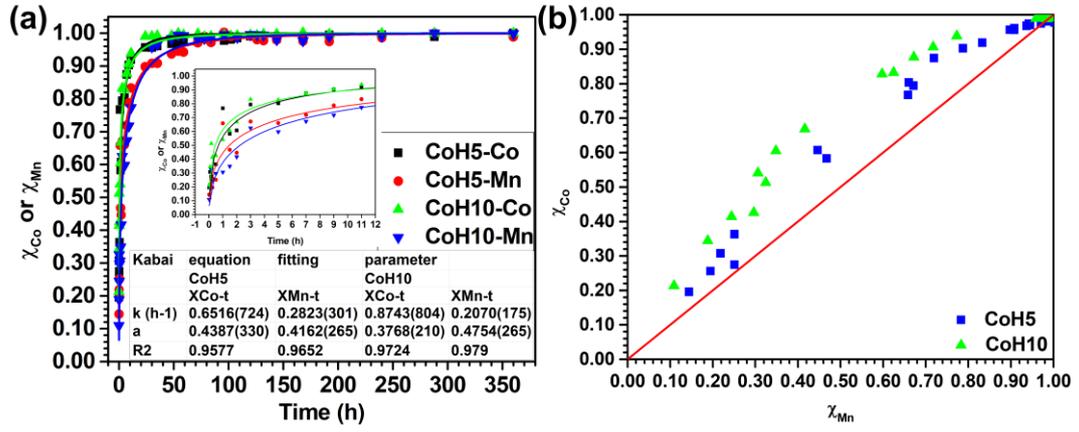
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722 **Fig. 4**

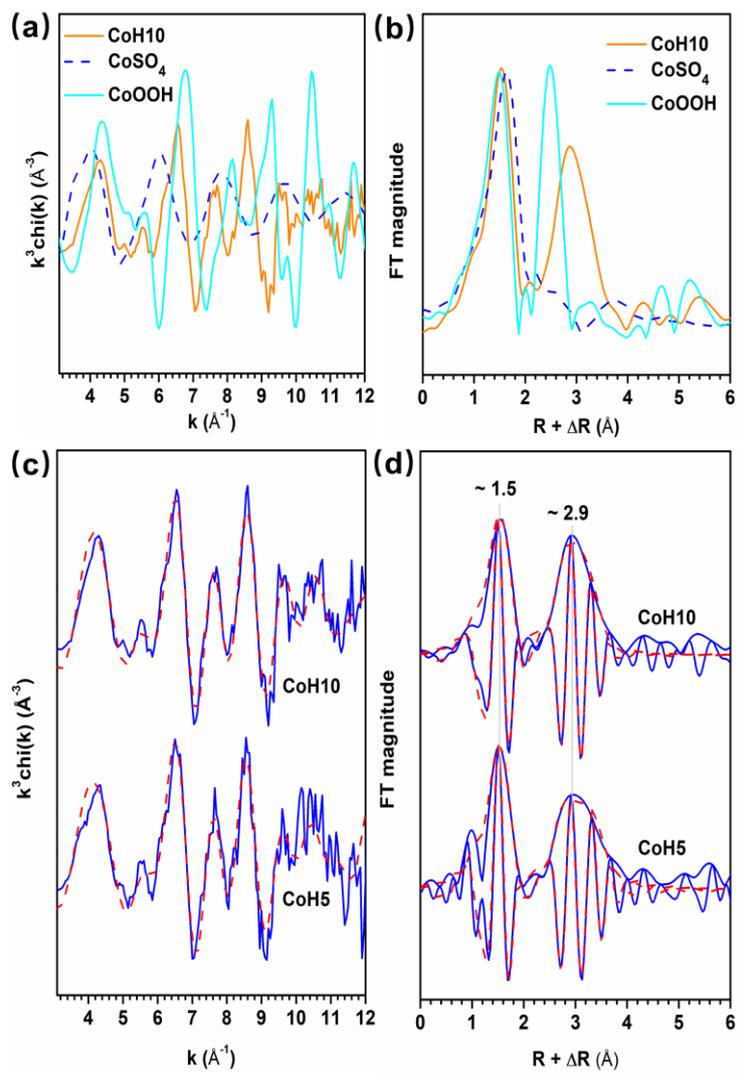
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725 **Fig. 5**

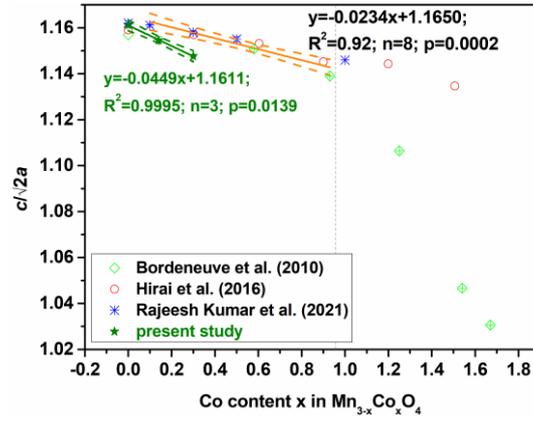
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727

728 **Fig. 6**

729



730

731 **Fig. 7**