XANES investigation of co-precipitated Fe and Cr fluorides catalytically active in heterogeneous dehydrochlorination

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In this X-ray absorption near-edge structure (XANES) study we focused our interest on co-precipitated Fe and Cr fluorides. Compounds with a low Cr content are catalytically active in the dehydrochlorination of 1,1,1-trichloroethane. XANES reveals for these samples an incorporation of a modified $CrF_{3-x}(OH)_x$ pyrochlore structure into the β-FeF_3 host lattice and an electron-deficient Cr 3d orbital, which may act as a Lewis acid site in the catalytic process.

Keywords: XANES, iron fluoride, chromium fluoride, Lewis acid sites, dehydrochlorination

1. Introduction

A broad variety of systems are used in heterogeneously catalyzed Cl/F exchange reactions, mostly based on aluminum, chromium or iron oxides and fluorides (pure or mixtures of them) [1–3]. In this X-ray absorption near-edge structure (XANES) study we focused our interest on the problem of chromium substitution of β-FeF_3. Compounds with a low Cr content are catalytically active in the dehydrochlorination of 1,1,1-trichloroethane, CH_3–CCl_3, at 130 °C. Additionally, α- and β-modifications of FeF_3 and CrF_3 as well as a mainly XRD amorphous and a highly crystalline $CrF_{3-x}(OH)_x$ sample with the pyrochlore structure were investigated.

2. Experimental

XANES measurements were performed on the EXAFS II beamline at HASYLAB (Hamburg, Germany) in the absorption mode. The beamline was equipped with a Si(111) double-crystal monochromator. Samples were pressed into pellets using polyethylene powder as a diluent. The edge jump was adjusted to 0.5–0.8 to avoid thickness effects. All K-edge XANES spectra were measured twice, energy-referenced to the respective metals, background corrected and normalized. K absorption edges of metal foils were referenced to values published by Kraft et al. [4]. We applied a linear background correction to all XANES spectra.

The nearly XRD amorphous $CrF_{0.39}(OH)_{2.61}\cdot(H_2O)_{0.8}$ xerogel (furthermore described as amorphous) and the co-precipitated Fe and Cr fluoride samples were synthesized by precipitation from ethanolic solutions of the respective nitrates in aqueous HF and subsequent heating of the precipitates under self-produced atmospheres at 300 °C [1]. At this temperature, all phases retain a small amount of water. A complete dehydration would result in a collapse of the pyrochlore structure.

The number of the co-precipitated Fe and Cr fluoride samples indicates the relative Fe content.

The pyrochlore sample with high crystallinity ($CrF_{0.38}(OH)_{2.62}\cdot(H_2O)_{1.77}$) was obtained by solvothermal synthesis from $CrF_3\cdot 3H_2O$ which was kept in ethanolic solution at 260 °C and 105 bar for 5 h. In this paper we will use the general formula $CrF_{3-x}(OH)_x$ for the pyrochlore phases, regardless of the amount of water of crystallization.

3. Results and discussion

For the identification of XANES peaks we adopted the scheme published by Grunes [5]. The first peak A denotes the pre-edge absorption, the dipole-forbidden 1s→3d transition. The dipole-allowed 1s→4p transition is assigned as peak C. The peaks due to multiple scattering processes are labeled with D.

For the β-FeF_3 sample we found a 1s→4p transition shift of -1.1 eV with respect to the α-phase (figure 1). A similar shift (-0.4 eV) is observed for the respective CrF_3 samples (figure 2). This difference is surprising because the stoichiometries and the first octahedral F-shell around the central atom are similar for the α- and the β-modifications in CrF_3 as well as in FeF_3. These shifts may be due to the crystallographic open structures of the β-phases in comparison to the α-structures, where less electron density is removed from the central atom by the next coordination spheres.

Furthermore, significant differences are found between the amorphous and the crystalline sample of the $CrF_{3-x}(OH)_x$ pyrochlore related structure, which are known to occur in a variable chemical composition. Following the ar-

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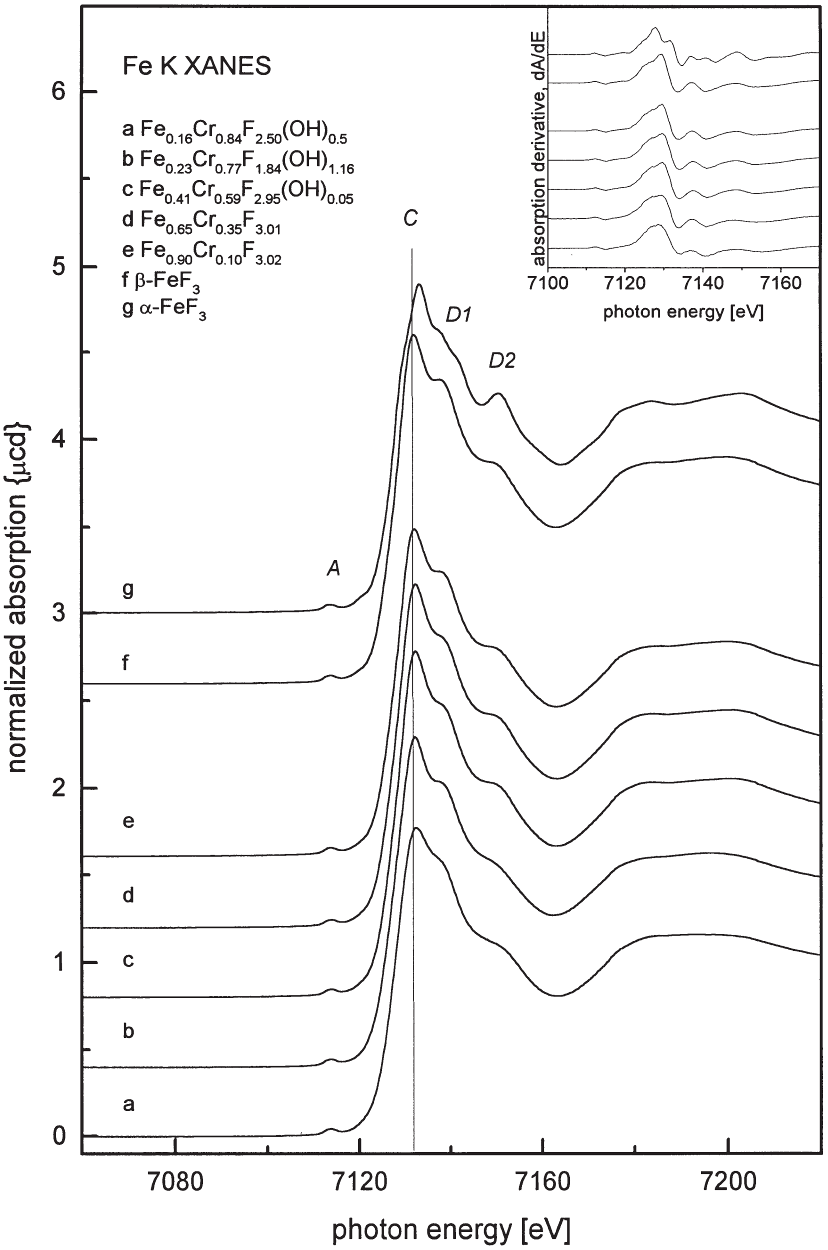

Figure 1. Fe K XANES spectra and their derivatives of co-precipitated Fe and Cr fluorides as well as α- and β-FeF_3.

guments of Belli et al. [6], in amorphous materials the solid state contributions to the near-edge structure are minimized, because these samples exhibit no long-range order. Finally, the near-edge structure is primarily determined by the local molecular cluster in amorphous materials. With our amorphous $CrF_{0.39}(OH)_{2.61}\cdot(H_2O)_{0.8}$ an almost structureless absorption behind the absorption edge was observed (figure 2, curve d). Therefore we can interpret the additional feature D1 in crystalline $CrF_{0.38}(OH)_{2.62}\cdot(H_2O)_{1.77}$ due to medium-range scattering, assuming that fluorine is statistically distributed (figure 2, curve c). The 1s→4p transition shift of 0.7 eV to lower photon energies obtained with crystalline $CrF_{3-x}(OH)_x$ in comparison to its amorphous modification may be due to its higher amount of water of crystallization. However, the energies of peak C of the $CrF_{3-x}(OH)_x$ samples with pyrochlore structure are much lower than those of the α- or the β-modifications of CrF_3.

In the modified β-FeF_3 system two principal groups of compounds were differentiated by their powder XRD pattern, catalytic activities for the CH_3–CCl_3 dehydrochlorination and the number of Lewis acid centers (cf. tables 1 and 2). One group is characterized by a low chromium content, high catalytic activity and a high number of Lewis acid sites. Exclusively in this case XRD proves the β-FeF_3 hexagonal tungsten bronze structure (HTB). The other group contains a high amount of chromium, reveals a low number of Lewis acid sites and low catalytic activity. Here, XRD reveals a $CrF_{3-x}(OH)_x$ pyrochlore structure [1]. Until now, there was no information on the chemical state and structure of the respective minority transition metal com-

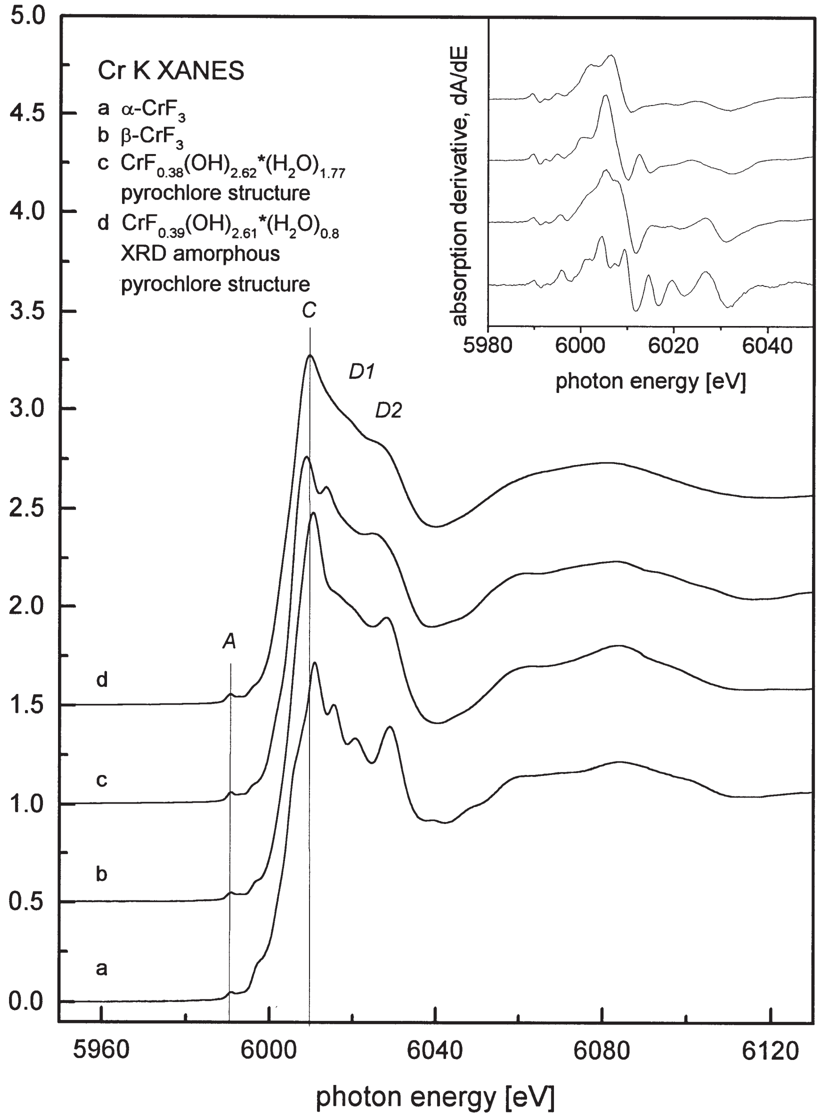

Figure 2. Cr K XANES spectra and their derivatives of chromium reference compounds.

Table 1
Summary of experimental facts and interpretation for the co-precipitated Fe and Cr fluorides.

Sample	Catalytic activity [1]	Lewis acid sites [1]	Powder XRD pattern [1]	Fe K$_\alpha$ XANES	Cr K$_\alpha$ XANES	Pre-edge Cr K$_\alpha$ XANES	Interpretation
$Fe_{0.16}Cr_{0.84}F_{2.50}(OH)_{0.5}$ $Fe_{0.23}Cr_{0.77}F_{1.84}(OH)_{1.16}$ $Fe_{0.41}Cr_{0.59}F_{2.95}(OH)_{0.05}$	low	low number	$CrF_{3-x}(OH)_x$ pyrochlore structure	β-FeF_3	$CrF_{3-x}(OH)_x$ pyrochlore structure	$CrF_{3-x}(OH)_x$ like	co-existing domains of $CrF_{3-x}(OH)_x$ and β-FeF_3
$Fe_{0.65}Cr_{0.35}F_{3.01}$ $Fe_{0.90}Cr_{0.10}F_{3.02}$	high	high number	β-FeF_3 hexagonal tungsten bronze	β-FeF_3	modified $CrF_{3-x}(OH)_x$ pyrochlore structure	shifted with respect to high Cr content group ⇒ e$^-$-deficient in Cr 3d orbital	incorporation of modified $CrF_{3-x}(OH)_x$ in β-FeF_3

pound in both groups of co-precipitated Fe and Cr fluorides.

The Fe K XANES spectra and their derivatives (figure 1) reveal for all modified β-FeF_3 samples a shape corresponding to that of the HTB β-FeF_3 sample. A slight shift (0.2 eV) of the white line C to higher photon energies with respect to pure β-FeF_3 is observed for all samples (one exception was Fe90, which gave results similar to β-FeF_3). The conclusion is that the presence of Cr has only little influence on the HTB structure in β-FeF_3.

The Cr K XANES spectra and their derivatives (figure 3) allow an identification of the state of Cr in the co-precipitated Fe and Cr fluorides. The above-mentioned classification in two groups of modified β-FeF_3 samples is further supported by a detailed study of Cr K XANES spectra (figures 3 and 4).

Table 2
Conversion of the dehydrochlorination of 1,1,1-trichloroethane to 1,1-dichloroethene at 130 °C with different catalysts [1].

Sample	Conversion of 1,1,1-trichloroethane (%)
$CrF_{0.38}(OH)_{2.62}\cdot(H_2O)_{1.77}$	0
$CrF_{0.39}(OH)_{2.61}\cdot(H_2O)_{0.8}$	5
$Fe_{0.16}Cr_{0.84}F_{2.5}(OH)_{0.5}$	4
$Fe_{0.23}Cr_{0.77}F_{1.84}(OH)_{1.16}$	9
$Fe_{0.41}Cr_{0.59}F_{2.95}(OH)_{0.05}$	10
$Fe_{0.65}Cr_{0.35}F_{3.01}$	75
$Fe_{0.90}Cr_{0.10}F_{3.02}$	58
β-FeF_3	24

For the catalytically inactive, high Cr content group (Fe16, Fe23 and Fe41) a less structured absorption is observed in the multiple scattering range (energy range 6010–6040 eV; figure 3, curves a–c). The same behavior is found for the amorphous $CrF_{3-x}(OH)_x$ xerogel reference sample (figure 2, curve d). Furthermore, their derivative spectra are similar, although the samples exhibit a different OH/F ratio. Obviously, Cr K XANES spectra are not strongly sensitive to OH/F exchange around the absorbing Cr, probably due to similar radii and atomic weights of OH and F.

In this group of samples the state of chromium is almost identical with that in the amorphous $CrF_{3-x}(OH)_x$ sample. Thus, the pyrochlore phase seems to be less affected by the β-FeF_3 domains. Hence, we deduce that β-FeF_3 and $CrF_{3-x}(OH)_x$ domains may co-exist. This interpretation is consistent with the low catalytic activity of these samples. Also the pure compounds ($CrF_{3-x}(OH)_x$ and β-FeF_3) possess only low catalytic activities (table 2).

In contrast, we found for the catalytically active, low Cr content group (Fe65 and Fe90) well-structured absorption

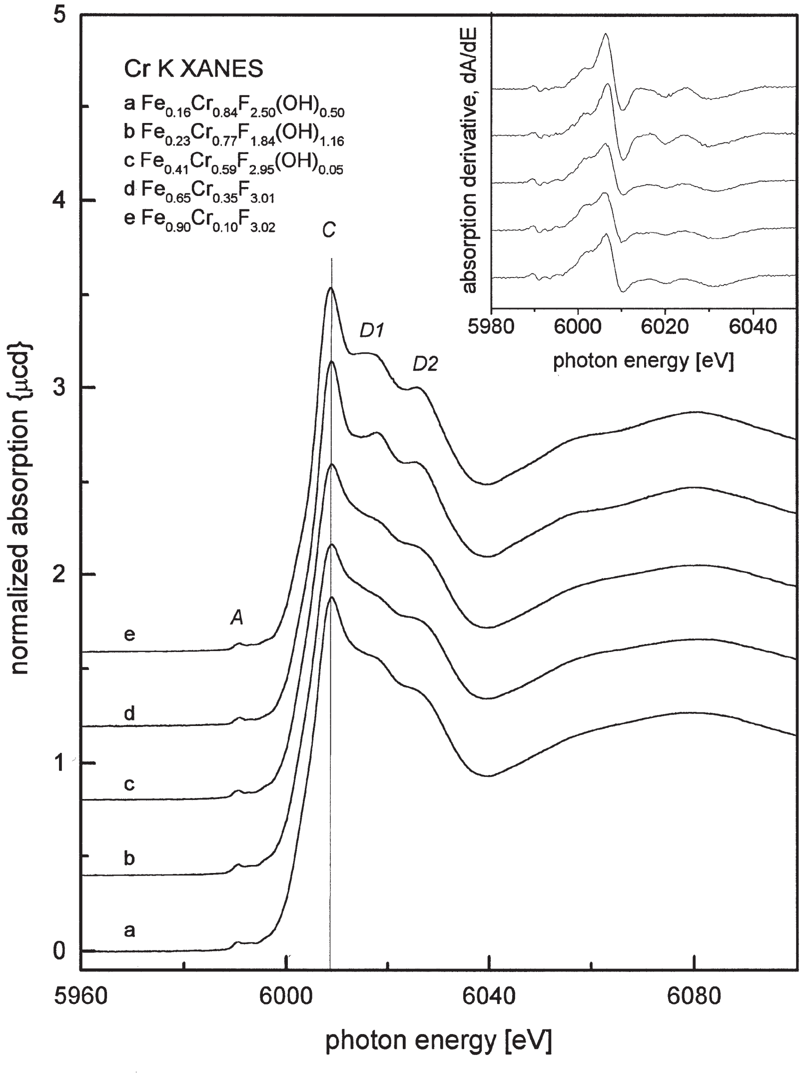

Figure 3. Cr K XANES spectra and their derivatives of co-precipitated Fe and Cr fluorides.

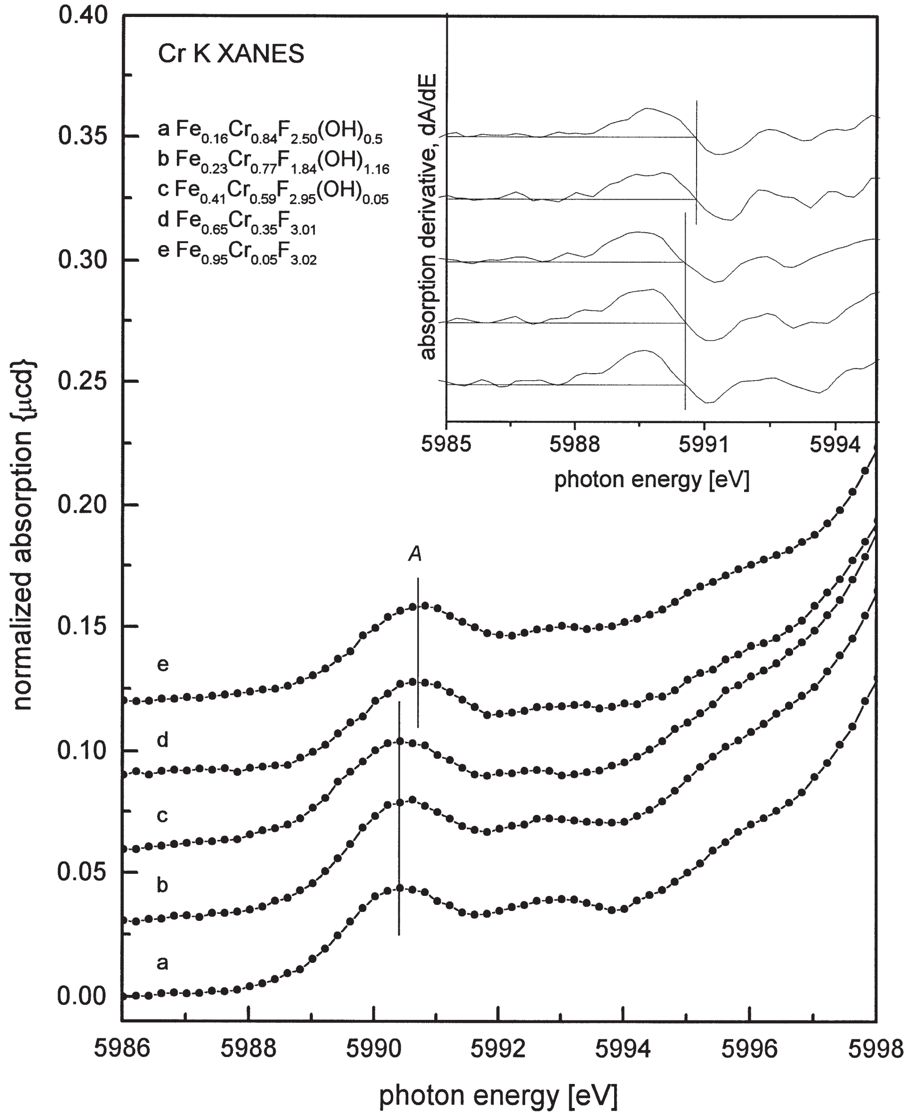

Figure 4. Expanded pre-edge region of Cr K XANES spectra and their derivatives of co-precipitated Fe and Cr fluorides.

spectra (figure 3, curves d, e). The absorption intensities of the three spectral features C, D1 and D2 are higher compared to the high Cr content group. This can be interpreted as a modified absorption of pyrochlore $CrF_{3-x}(OH)_x$. The chemical state of chromium seems to be influenced by the β-FeF_3 lattice (figure 3). This is an indication for an insertion of Cr into the β-FeF_3 lattice. The structure D1 is broadened for Fe90, the sample with the lowest Cr content.

The energy of peak C of all co-precipitated Fe and Cr fluorides coincides with the group of the pyrochlore structure samples. Furthermore, the derivative spectra of all co-precipitated Fe and Cr fluorides differ clearly from the β-CrF_3 sample and reveal the shape similar to the variable pyrochlore structure samples (figure 2, curves c, d). So, we found Cr to be involved into a pyrochlore structure for all modified β-FeF_3 samples.

In combination with the high F contents measured by the method of Seel [1,7], it can be concluded that Cr in β-FeF_3 does not remarkably trend to hydrolysis which is characteristic of Cr in pyrochlore-CrF_3. Pure CrF_3 is not known to have a pyrochlore structure and the β-FeF_3 lattice seems to stabilize the pyrochlore structure of $CrF_{3-x}(OH)_x$ with high fluorine contents.

Furthermore, the pre-edge features A of Cr K absorption, originating from dipole-forbidden 1s→3d transition, are shifted by 0.3 eV to higher photon energies for the lower Cr-containing group (figure 4). This can be interpreted as a partial electron deficiency in the Cr 3d orbital due to charge transfer from the Cr 3d orbital to the β-FeF_3 lattice. The charge transfer from Cr to Fe correlates with their different electronegativities, 1.6 and 1.8, respectively.

4. Conclusion

Summarizing the experimental facts (cf. table 1), we found that at low Cr concentrations the β-FeF_3 lattice incorporates Cr, where it exists in a modified $CrF_{3-x}(OH)_x$

pyrochlore structure. In these samples, chromium ions become affected by charge transfer from its Cr 3d orbital to the β-FeF_3 lattice. The electron-deficient Cr 3d orbital may act as a Lewis acid site in the catalytic process.

On the other hand, exceeding a critical limit of Cr content (roughly 50 mol% of cations), a formation of coexisting, only weak interacting $CrF_{3-x}(OH)_x$ and β-FeF_3 phases is favored under the given conditions of preparation.

Considering the high F contents, especially found for the samples with lower Cr contents, it seems that the β-FeF_3 lattice stabilizes the CrF_3 in the pyrochlore structure.

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