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Article

Study of the Structural, Electronic, and Magnetic Properties of the Barium-Rich Iron(IV) Oxides, Ba_2FeO_4 and Ba_3FeO_5

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Crystals of Ba_2FeO_4 and Ba_3FeO_5, grown from a "self-sealing" KOH–$Ba(OH)_2$ flux, have been characterized by single-crystal X-ray diffraction, Mössbauer spectroscopy, and magnetic measurements. Ba_2FeO_4 forms nonmerohedral twinned crystals with the monoclinic space group $P2_1/n$, $a = 6.034(2)$ Å, $b = 7.647(2)$ Å, $c = 10.162(3)$ Å, $\beta = 92.931(6)°$, and $Z = 4$. Ba_3FeO_5 crystallizes in the orthorhombic space group *Pnma*, with $a = 10.301(1)$ Å, $b = 8.151(1)$ Å, $c = 7.611(1)$ Å, and $Z = 4$. While both compounds feature discrete FeO_4^{4-} tetrahedra, the anion found in Ba_2FeO_4 has shorter Fe–O bonds and is significantly distorted relative to the Ba_3FeO_5 anion. An iron valence of 4+ was confirmed by magnet susceptibility measurements and by the low-temperature isomer shifts of –0.152 and –0.142 mm/s relative to α-iron for Ba_2FeO_4 and Ba_3FeO_5, respectively.

Introduction

Alkali and alkaline-earth ferrates that contain iron in oxidation states higher than iron(III) have garnered much attention in recent years because they can possess both unusual electronic properties[1] and solid-state structures.[2] Furthermore, these ferrates can be used as oxidizing agents[3] and battery cathodes.[4] To date, studies of the structures and physical properties of high oxidation state barium iron oxides, a subset of the aforementioned ferrates, have focused[5] on $BaFeO_4$ and the oxygen-deficient perovskites,[6] $BaFeO_{3-x}$. However, little is known about the barium-rich iron(IV) oxides, Ba_2FeO_4 and Ba_3FeO_5. Scholder et al. reported[7] that Ba_2FeO_4 and Ba_3FeO_5 powders can be synthesized by dehydrating the barium iron(III) hydroxides with the appropriate Ba/Fe ratios at 700 °C under a dynamic atmosphere of O_2. The powder patterns of Ba_2FeO_4 and Ba_3FeO_5 were reported[8] to resemble those of β-Ca_2SiO_4 and Cs_3CoCl_5, but no detailed structural data were given. Furthermore, no information on the electronic or magnetic properties of Ba_2FeO_4 and Ba_3FeO_5 has been reported. In this article, we report a new molten KOH–$Ba(OH)_2$ flux synthesis that yields large crystals of Ba_2FeO_4 and Ba_3FeO_5. The compounds have been characterized by single-crystal X-ray diffraction, SQUID magnetometry, and Mössbauer spectroscopy.

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Table 1. Crystallographic Data for Ba_2FeO_4

Ba_2FeO_4
$a = 6.034(2)$ Å
$b = 7.647(2)$ Å
$c = 10.162(3)$ Å
$\beta = 92.931(6)°$
$V = 468.3(3)$ Å^3
$Z = 4$

fw = 394.53
$P2_1/n$ (No. 14)
$T = 138$ K
$\lambda = 0.71069$ Å
$D_{calcd} = 5.596$ g/cm^3
μ(Mo K) = 19.578 cm^{-1}
R1^a = 0.0478
wR2^b = 0.1143

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2 = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Crystallographic data for Ba_3FeO_5

Ba_3FeO_5
$a = 10.301(1)$ Å
$b = 8.151(1)$ Å
$c = 7.611(1)$ Å
$V = 639.05(11)$ Å^3
$Z = 4$

fw = 547.87
Pnma (No. 62)
$T = 157$ K
$\lambda = 0.71069$ Å
$D_{calcd} = 5.694$ g/cm^3
μ(Mo K) = 20.41 cm^{-1}
R1^a = 0.0471
wR2^b = 0.0925

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2 = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Experimental Section

Crystal Growth. Anhydrous $Ba(OH)_2$ was prepared by dehydrating $Ba(OH)_2 \cdot 8H_2O$ (Strem, 98+%) at 280 °C for 1 h. Ba_2FeO_4 was prepared by heating a mixture of 1.9 g $Ba(OH)_2$, 2.5 g of KOH (Johnson Mathey, Ultrapure), and 0.4 g of Fe_2O_3 (Alfa Aesar, 99.945%) in a 20 mL alumina crucible which had an alumina lid. Ba_3FeO_5 was prepared from 2.8 g $Ba(OH)_2$, 2.5 g of KOH, and 0.4 g of Fe_2O_3 in a similar crucible. In each case, the reaction mixture was heated from room temperature to 750 °C over 5 h, maintained at 750 °C for 5 h, and then slowly cooled to 600 °C over a period of 32 h. The furnace was then shut off, and the crucible and its contents were allowed to cool to room temperature. In the process of heating, the molten flux crept up the sides of the crucible and sealed the lid. Removal of the lid revealed a bed of loose crystals on the bottom of the crucible. The crystals were isolated by hand in an inert atmosphere box as both Ba_2FeO_4 and Ba_3FeO_5 are moisture sensitive.

Structure Determination for Ba_2FeO_4. A nonmerohedrally twinned dataset was collected with a SMART CCD area detector. Using GEMINI,[9] the reflections were indexed, and the second twin component was found to be related by a 180° rotation about the [100] axis. The masses of the two twins were found to have a ratio of approximately 2:1. Data from the greater twin were integrated using SAINT[10] to a maximum 2θ value of 50.27°. An empirical absorption correction was applied using SADABS.[11] The data were converted to HKLF 5 format using ROTWIN (V. G. Young, Jr.). About $^2/_5$ of the data had partially overlapped reflections from both twin components. The structure was solved by direct methods and expanded using Fourier techniques.[12] The final cycle of full-matrix least-squares refinement against F^2 was based on 767 unique reflections and 47 variable parameters. The barium and iron atoms were refined anisotropically while the oxygens were refined isotropically. Crystal data are given in Table 1.

Structure Determination for Ba_3FeO_5. Data were collected with a SMART CCD area detector and integrated by the program SAINT. A face indexed absorption correction was applied using XPREP,[13] and an empirical correction was applied using SADABS. The structure was solved by direct methods. The final cycle of full-matrix least-squares refinement against F^2 was based on 1377 unique reflections and 50 variable parameters. All atoms were refined anisotropically. Crystal data are given in Table 2.

Mössbauer Spectroscopy. Mössbauer spectra were measured between 78 and 295 K on a constant-acceleration spectrometer which utilized a room-temperature rhodium matrix cobalt-57 source and was calibrated at room temperature with α-iron foil. The estimated absolute errors are ±0.005 mm/s for the isomer shifts and ±0.01 mm/s for the quadrupole splittings and line widths.

Magnetic Measurements. Magnetic susceptibility measurements were obtained as a function of temperature on a Quantum Design SPMS SQUID. Data were collected on samples contained in gelatin capsules and corrected for the associated diamagnetism.

Results and Discussion

The structure determination of Ba_2FeO_4 from a twinned crystal revealed it to be isostructural with β-Ca_2SiO_4; thus, it is composed of isolated FeO_4^{4-} tetrahedra that are coordinated in an irregular manner by nine barium(II) ions. A schematic diagram of the structure is shown in Figure 1a. The related Ba_2MO_4 compounds, where M is Ti, V, Cr, or Co, also consist of discrete MO_4^{4-} tetrahedra.[14,15] This adherence to a single structural motif is in contrast to the 2:1:4 strontium metalates. Sr_2CrO_4 has isolated CrO_4^{4-} tetrahedra,[16] and Sr_2VO_4 has $V_2O_8^{8-}$ dimers,[17] whereas Sr_2TiO_4 and Sr_2FeO_4 have the K_2NiF_4 structure.[18] Apparently, the large ionic radius of barium(II), which effectively isolates the MO_4^{4-} tetrahedra and prevents oxo-bridging, is the primary reason for the isostructural nature of the Ba_2MO_4 compounds.

Ba_3FeO_5 was reported[8] to be isostructural with Cs_3CoCl_5 which is tetragonal with space group *I*4/*mcm*. We have found that Ba_3FeO_5 precipitated from the molten KOH−$Ba(OH)_2$ eutectic is orthorhombic with space group *Pnma* and is isostructural[19] with Ba_3FeS_5. A schematic diagram of the structure is shown in Figure 1b. As in Ba_2FeO_4, Ba_3FeO_5 consists of isolated FeO_4^{4-} tetrahedra, but there is an additional BaO per formula unit. This additional BaO results in a fifth oxygen ion that does not bond to iron(IV) but is coordinated by six barium(II) nearest neighbor ions, which yield a distorted octahedral coordination environment.

The prominent structural features of Ba_2FeO_4 and Ba_3FeO_5 are the isolated FeO_4^{4-} tetrahedral anions. The structure

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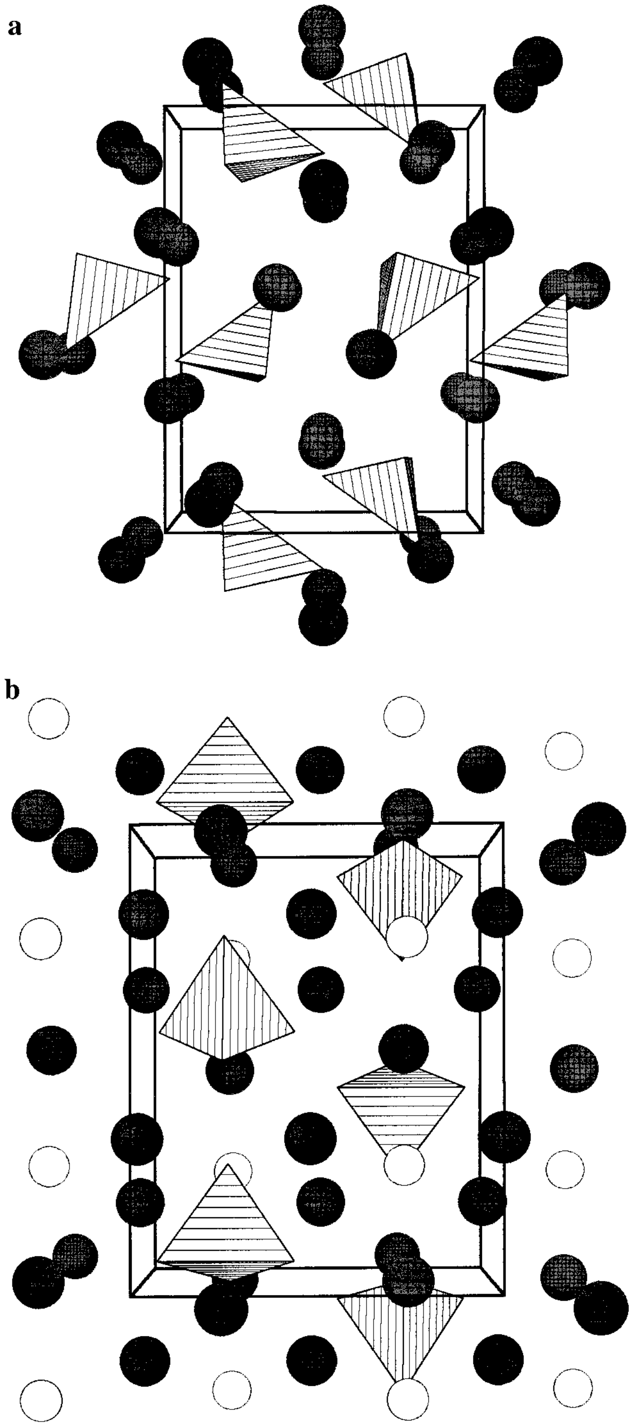

Figure 1. (a) X-ray crystal structure of Ba_2FeO_4 projected along the [100] direction. Barium atoms are shown as black circles; FeO_4^{4-} anions are shown as polyhedra. (b) X-ray crystal structure of Ba_3FeO_5 projected along the [001]. Barium atoms are shown as black circles, oxygen atoms are shown as white circles, and FeO_4^{4-} anions are shown as polyhedra.

of this anion was recently characterized[2] for the first time in Na_4FeO_4 and was found to be compressed along a C_2 axis. The compression was attributed to the d^4 electron configuration of iron(IV); that is, the lowered symmetry lifts the degeneracy of the t_2 orbital resulting in a net energetic stabilization, the well-known Jahn−Teller effect.

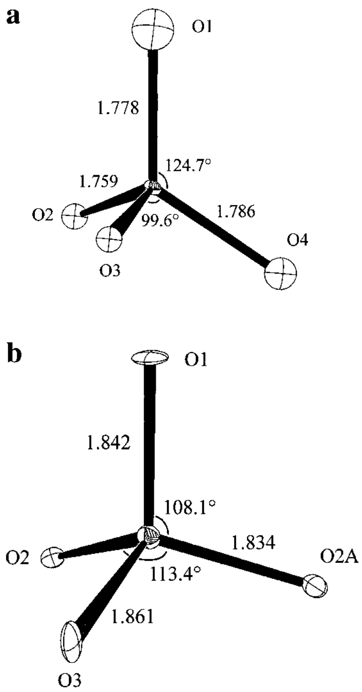

Figure 2. (a) ORTEP plot of the FeO_4^{4-} anion in Ba_2FeO_4 (50% thermal ellipsoids). Max and min angles are labeled. (b) ORTEP plot of the FeO_4^{4-} anion in Ba_3FeO_5 (50% thermal ellipsoids). The ion has crystallographically imposed *m* symmetry. Max and min angles are labeled.

The FeO_4^{4-} tetrahedra found in Ba_2FeO_4, see Figure 2a, are distorted in a manner similar to the distortion found[2] in Na_4FeO_4. The anion has approximate D_{2d} symmetry with O−Fe−O angles ranging from 99.6° to 124.7°. This is a distortion of ±13.9% from the angle of 109.5° for perfect tetrahedral symmetry. In contrast, the FeO_4^{4-} tetrahedra found in Ba_3FeO_5, see Figure 2b, are much closer to ideal, as they are only distorted by ±3.6% from perfect tetrahedral symmetry. This conflicting behavior suggests that interatomic forces other than Jahn−Teller stabilization must determine the degree of distortion of these tetrahedra. Anions that are not subject to the Jahn−Teller effect will sometimes distort from their idealized geometry. The driving forces for these distortions are Coulombic packing interactions within the crystal, that is, *matrix effects*.[20] This argument is buttressed by several examples of distorted $3d^0$ and $3d^5$ tetrahedra.[14,21] In Ba_2FeO_4 and Ba_3FeO_5, the efficacy of the Jahn−Teller effect is, no doubt, diminished relative to, say, the tetragonal distortion observed in octahedral complexes because of the nonbonding character of the t_2 orbitals in pseudotetrahedral symmetry. In short, while the $3d^4$ electronic structure may provide an impetus for distortion, matrix effects play the predominate role in determining the degree of distortion in these compounds.

The average Fe−O bond length in Ba_2FeO_4 is 1.78 Å, remarkably shorter than the 1.84 Å average bond length found in Ba_3FeO_5. This disparity is likely a consequence of packing effects, but a small reduction in formal valence could also result from the longer bonds in Ba_3FeO_5. The relationship between metal−oxygen bond lengths and valence is

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Table 3. Mössbauer Spectral Parameters

compound	T,K	δ, mm/s[a]	ΔE_Q, mm/s	Γ, mm/s
Ba_2FeO_4	295	−0.244	0.33	0.34
	225	−0.185	0.34	0.37
	155	−0.169	0.35	0.37
	85	−0.152	0.36	0.35
Ba_3FeO_5	295	−0.225	0.35	0.29
	240	−0.204	0.34	0.30
	190	−0.199	0.37	0.30
	140	−0.168	0.40	0.30
	90	−0.150	0.39	0.31
	78	−0.142	0.39	0.32

[a] The isomer shifts are given relative to room temperature α-iron foil.

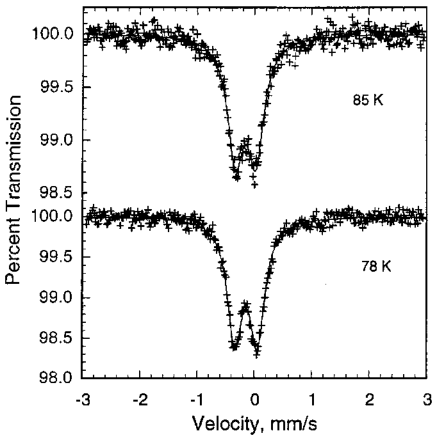

Figure 3. Mössbauer spectra of Ba_2FeO_4, top, and Ba_3FeO_5, bottom, obtained at 85 and 78 K, respectively.

often described by using bond valence theory.[22] By using the procedure outlined by Brown,[23] we have calculated the bond valence parameter $R_o = 1.798$ for Fe^{4+}, a calculation which is based both on our crystallographic data and on existing data.[24] This yields an estimated valence of +4.2 and +3.6 for iron sites in Ba_2FeO_4 and Ba_3FeO_5, respectively. This method likely overestimates the deviation from the formal valence of +4, but it is worth noting that these values are in reasonable agreement with the expected tetravalence.

Iron-57 Mössbauer spectroscopy is also widely used to estimate the valence state of iron, but the isomer shift of tetrahedral oxoferrate(IV) has not been previously reported. Examples of octahedral oxoferrates(IV) are rare but are known to have room-temperature isomer shifts between −0.20 and +0.05 mm/s relative to α-iron.[25] The temperature dependence of the iron(IV) isomer shift is also of considerable interest because iron(IV) sites in other alkaline earth ferrates have been shown[1] to undergo charge disproportionation into Fe^{III} and Fe^{V} at low temperature.

The low-temperature isomer shifts of −0.152 and −0.142 mm/s relative to α-iron for Ba_2FeO_4 and Ba_3FeO_5, respectively (see Table 3), obtained from the experimental Mössbauer spectra (see Figure 3) are in agreement with the value of approximately −0.20 mm/s that we would predict from the empirical relationship[26] between the oxidation state, coordination number, and the iron-57 isomer shift for tetrahedral oxoferrate(IV). A calculation[27] of the iron(IV) Wigner−Seitz cell volumes for Ba_2FeO_4 and Ba_3FeO_5 yields values of 1.918 and 2.367 Å^3, respectively. As expected, Ba_3FeO_5 with the larger Wigner−Seitz cell volume has the less negative isomer shift. On the basis of the spectral isomer shifts, the formal valence for iron in Ba_2FeO_4 is slightly greater than that in Ba_3FeO_5, an increase which is consistent with our bond valence theory oxidation state estimates. No charge disproportionation is observed down to 85 K. As expected on the basis of the small distortion of the isolated FeO_4^{4-} tetrahedral anions, the quadrupole splittings of both Ba_2FeO_4 and Ba_3FeO_5 are small. Surprisingly, the absolute value of the splitting of Ba_2FeO_4 is slightly smaller than that of the less distorted Ba_3FeO_5. However, the signs of the two quadrupole splittings may be different.

The utility of Mössbauer spectroscopy is underscored if one considers the case of Ba_3FeS_5 which has the same structure as Ba_3FeO_5. On the basis of its stoichiometry, Ba_3FeS_5 should contain iron(IV). Magnetic results were inconclusive in determining the iron oxidation state, but a comparison of the Ba_3FeS_5 isomer shifts[19] of 0.17 and 0.26 mm/s at 300 and 78 K, respectively, with known Mössbauer spectral isomer shifts clearly indicated the presence of tetrahedral iron(III) in Ba_3FeS_5. Thus, Goodenough et al. described[28] Ba_3FeS_5 as $BaS{\cdot}Ba^{2+}{}_2[Fe^{3+}(S_4)^{7-}]$; that is, the iron is reduced and gives rise to a hole in the S^{2-} $3p^6$ band. A similar behavior for Ba_2FeO_4 or Ba_3FeO_5 is unlikely because, as is well-known, the tetrahedral O^{2-} ligand environment can stabilize iron valence states up to +6; nevertheless, the Mössbauer isomer shift provides a valuable confirmation of the iron(IV) oxidation state in both Ba_2FeO_4 and Ba_3FeO_5. Therefore, bond valence theory and Mössbauer spectroscopy both support an approximate d^4 configuration, with Ba_2FeO_4 achieving a slightly greater valence than Ba_3FeO_5.

A plot of the molar magnetic susceptibility as a function of temperature for Ba_2FeO_4, see Figure 4, shows a maximum at 25 K, a maximum which indicates the onset of short-range antiferromagnetic ordering. A Curie−Weiss law fit of the inverse susceptibility above 60 K yields a Weiss constant of −50 K, a negative value which is indicative of antiferromagnetic interactions. The Curie constant of 2.99 emu K/mol leads to an effective magnetic moment, μ_{eff}, of 4.89 μ_B, a value which is which is in excellent agreement with the theoretical spin only moment of 4.90 μ_B.

Though both ferrates contain similar FeO_4^{4-} anions, the magnetic behavior of Ba_3FeO_5 is rather different from that of Ba_2FeO_4. A plot of the inverse susceptibility versus temperature for Ba_3FeO_5 is also shown in Figure 4. The data were fit using the Curie−Weiss relationship, yielding a Curie

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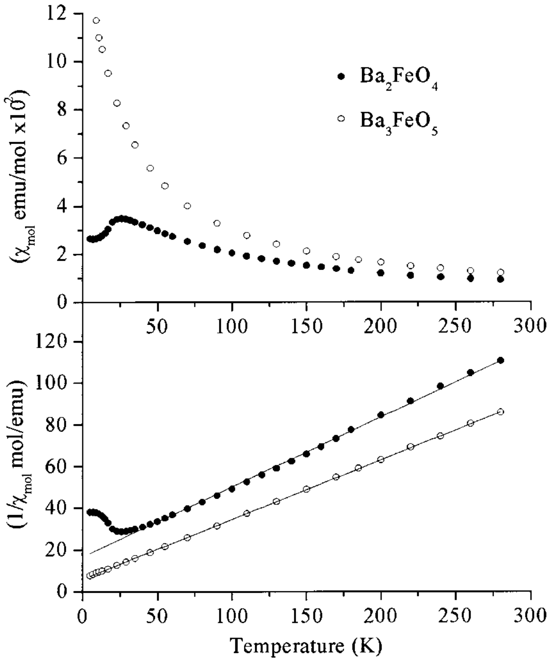

Figure 4. Molar magnetic susceptibility of Ba_2FeO_4 and Ba_3FeO_5 (top) as a function of temperature. The inverse molar magnetic susceptibility of Ba_2FeO_4 and Ba_3FeO_5 (bottom) as a function of temperature and its fit with the Curie−Weiss law.

constant of 3.50 emu K/mol and a Weiss temperature of −21 K. Thus, Ba_3FeO_5 is paramagnetic down to 5 K, but at temperatures below 5 K, a Neel temperature is anticipated. The Curie constant yields an effective magnetic moment of 5.29 μ_B. The deviation from the spin-only value likely results from spin−orbit coupling that is quenched in the distorted anion.

Ba_2FeO_4 exhibits antiferromagnetic ordering below 25 K whereas Ba_3FeO_5 is paramagnetic down to 5 K. Thus, the intermolecular coupling is significantly reduced in Ba_3FeO_5 relative to that in Ba_2FeO_4. This magnetic dilution results from the increased interanionic spacing that accompanies the incorporation of an additional BaO per formula unit. The reduction in cooperative interaction is in accord with the crystallographic structures which reveal that the closest iron−iron distances are 4.752 and 5.254 Å in Ba_2FeO_4 and Ba_3FeO_5, respectively. Most likely, the magnetic exchange pathways involve two intervening oxygen dianions; Fe−O•••O−Fe. The shortest intertetrahedral O•••O distance in Ba_2FeO_4 is 3.221 Å, whereas, because the tetrahedra are more isolated, the shortest O•••O distance in Ba_3FeO_5 is 3.384 Å. Interestingly, the closest nonbonding Fe•••O distance is 3.834 Å in Ba_2FeO_4 as compared to 3.686 Å in Ba_3FeO_5 which suggests that coupling through a single intervening oxygen, that is, Fe−O•••Fe, is not the dominant exchange pathway.

In conclusion, the structures of Ba_2FeO_4 and Ba_3FeO_5 have been found to contain discrete FeO_4^{4-} anions with differing bond lengths and degrees of distortion: a consequence of matrix effects. The negative Mössbauer effect isomer shifts observed for the tetrahedral oxoferrate(IV) ion are consistent with the presence of iron(IV). Ba_3FeO_5 is paramagnetic down to 5 K but has a negative Weiss temperature, whereas Ba_2FeO_4 orders antiferromagnetically at 25 K. The weaker magnetic exchange coupling in Ba_3FeO_5 results from the magnetic dilution that accompanies the inclusion of an additional BaO in the formula unit.

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Supporting Information Available: X-ray crystallographic files, in CIF format, are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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