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Synthesis and structure of $BaKFeO_3$: a new quaternary oxide with 1-D ferrate chains

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Abstract

Amber-colored single crystals of the quaternary oxide $BaKFeO_3$ were synthesized from a mixture of Fe_2O_3, KOH and $Ba(OH)_2$ heated at 750°C for 5 h then cooled slowly. The structure was determined by single-crystal X-ray diffraction (space group *Cmca*; $a = 5.804(1)$ Å, $b = 11.528(1)$ Å, $c = 12.776(1)$ Å; $Z = 8$, $R_1 = 0.0376$, $wR_2 = 0.0996$). The structure is comprised of $[FeO_3^{3-}]^{\infty}$ chains of corner-sharing iron-oxo tetrahedra that are isolated from one another by interspersed Ba and K cations. The iron coordination environment is moderately distorted from perfect tetrahedral symmetry and the Fe–O–Fe bond angles are 152.8°. Magnetic susceptibility data show a pronounced zero-field cooling effect that suggests strong coupling from 5 K to above room temperature.

1. Introduction

Investigations into the structural chemistry of alkali iron(III) oxides has uncovered numerous compounds derived from tetrahedral FeO_4 units [1–8]. In general, the dimensionality of these iron-oxo structures depends on the ratio of alkali metal to iron cations in the compounds. For example, β-$NaFeO_2$ has a three-dimensional structure based on FeO_4 tetrahedra that share all corners, whereas alkali-rich Na_5FeO_4 can be considered zero-dimensional, as it has isolated FeO_4^{5-} tetrahedra [9].

Intermediate in this structural series are the one-dimensional iron(III) oxides. A few examples with the general form A_3FeO_3 (where A is a combination of Na, K, Rb, Cs) have been prepared by Hoppe and co-workers [5,6,8]. These compounds are based on FeO_4 tetrahedra that share two corners, leading to $[FeO_3^{3-}]^{\infty}$ chains with linear Fe–O–Fe bonds connecting the adjacent metal centers. The alkali metal cations are interspersed between the chains, isolating them from one another.

We have recently prepared an alkali/alkaline earth iron oxide, $BaKFeO_3$, which is related to Hoppe's alkali metal iron oxide chain compounds, using a molten hydroxide synthetic approach. This technique has proven to be a useful alternative to traditional solid state syntheses for the growth of single crystals of low-dimensional transition metal oxides [10], but the molten hydroxide synthesis of iron oxides has not been widely explored [11,12]. We report here the preparation, structure and low-temperature magnetic behavior of $BaKFeO_3$.

2. Experimental

A mixture of 0.93 g $Ba(OH)_2$, 1.50 g KOH and 0.40 g α-Fe_2O_3 was added to a 20 mL alumina crucible, which was capped with an alumina lid. The crucible was placed in a box furnace and heated from room temperature to 750°C in 5 h, then soaked at 750°C for 5 h. The reaction mixture was steadily cooled to 600°C over the course of 32 h. Power to the furnace was then terminated and the crucible and its contents were allowed to cool to room temperature. The lid, which was sealed to the crucible by solidified flux, was removed by hand, revealing a bed of amber crystals on the bottom of crucible. Single crystals were isolated by hand in an inert atmosphere because $BaKFeO_3$ decomposes if exposed to moisture.

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Table 1
Crystal data for $BaKFeO_3$

Crystal color, habit	Amber, prismatic
Crystal size	$0.15 \times 0.25 \times 0.40\,mm^3$
Crystal system, space group	Orthorhombic, *Cmca*
Unit cell dimensions	$a = 5.804(1)\,Å$, $\alpha = 90°$ $b = 11.528(1)\,Å$, $\beta = 90°$ $c = 12.776(1)\,Å$, $\gamma = 90°$
Volume	$854.81(4)\,Å^3$
Z, Calculated density	8, $4.356\,g/cm^3$
Formula weight	280.29
Reflec. collected/unique	1773/417 [R(int) =0.0382]
No. variables	36
Goodness-of-fit on F^2	1.146
Final *R* indices ($I > 2.00\sigma(I)$)	$R_1 = 0.0376$, $wR_2 = 0.0996$
R indices (all data)	$R_1 = 0.0395$, $wR_2 = 0.1006$

Table 2
Atomic coordinates and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $BaKFeO_3$

	x	y	z	U_{eq}
K1	0.0000	0.0476 (2)	0.1426 (2)	0.008 (1)
Ba1	0.0000	0.3568 (1)	0.0804 (1)	0.007 (1)
Fe1	0.0000	0.2317 (1)	0.3361 (1)	0.005 (1)
O1	0.0000	0.3307 (6)	0.4515 (6)	0.011 (2)
O2	0.0000	0.0758 (7)	0.3767 (5)	0.013 (2)
O3	0.2500	0.2698 (6)	0.2500	0.007 (1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

X-ray diffraction measurements were made on a single crystal of $BaKFeO_3$ with a CCD area detector with graphite monochromated Moκ radiation. Cell constants were determined from 1773 reflections with $I > 10\ \sigma$, corresponded to an orthorhombic cell with $a = 5.804(1)\,Å$, $b = 11.528(1)\,Å$ and $c = 12.776(1)\,Å$. Integration on a primitive cell gave poor correlation statistics but strong correlations were calculated for a C-centered cell. The space group *Cmca* was assigned upon review of the systematic absences and an empirical absorption correction was applied based on comparison of redundant and equivalent reflections using SADABS [13]. The structure was solved by direct methods and expanded using Fourier techniques [14]. Anisotropic temperature factors were included in the final refinement for all atoms. Selected refinement details, including cell parameters, are given in Table 1. Atomic coordinates and isotropic displacement parameters are listed in Table 2. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-412877.

Quantitative elemental microanalysis performed with a JEOL 6300 scanning electron microscope equipped with an energy dispersive X-ray spectrometer gave a Ba/K/Fe ratio of 1:1:1. Magnetizations vs. field data were collected on a Quantum Design MPMS SQUID. Measurements were made on samples contained in gelatin capsules and data were corrected for the associated diamagnetism of the capsules.

3. Results and discussion

3.1. Synthesis

A preliminary study of the solvation and crystallization properties of iron oxides in a KOH–$Ba(OH)_2$ eutectic revealed that 60/40 mixtures of KOH/$Ba(OH)_2$ melted at approximately 350°C upon heating. When α-Fe_2O_3 was added to the molten flux, it readily dissolved and turned the flux a brown-black color. A marked decrease in metal solubility, signified by the precipitation of dark brown powder on the sides of the crucible, was observed above 550°C as hydroxide decomposed to oxide and water vapor. These reactions, carried out in air in open alumina crucibles, typically produced heterogeneous powders that were difficult to characterize.

The efficacy of this flux for the growth of high-quality crystals was greatly improved when the crucible was covered with an alumina lid. Capped 20 mL alumina crucibles with more than 2 g of $Ba(OH)_2$–KOH flux routinely sealed shut when heated above 600°C and, in the process, single crystals precipitated at the bottom of the crucible. The seal at the rim of the crucible was primarily composed of K_2CO_3 that presumably was a product of KOH decomposition followed by a reaction with atmospheric CO_2. However, there were no indications that atmospheric CO_2 was incorporated into the crystalline product.

The improved crystal growth conditions realized for the capped reactions can be attributed to several factors. First, the lid helps retain water produced during the decomposition of the oxides to hydroxides and thus reduces the rate of dehydration. Consequently the flux slowly saturates with oxide, favoring the growth of high-quality crystals. Second, the flux remains acidic (Lux-Flood formalism) at significantly higher reaction temperatures. This allows the reactants to diffuse and intimately mix. Third, the seal isolates the flux from significant thermal gradients and atmospheric CO_2 while heating. Additionally, upon cooling the seal isolates air sensitive products from atmospheric moisture.

3.2. Crystal structure

The crystal structure of $BaKFeO_3$, shown in Fig. 1, is isotypic with Rb_2TiO_3 [15,16], A_2CoO_3 (A = Cs, K, Rb) [17], Ca_2PN_3 [18] and Ba_2VN_3 [19]. This structure type has the general form $ABMX_3$, where A and B are alkali or alkaline earth cations, M is a transition metal or

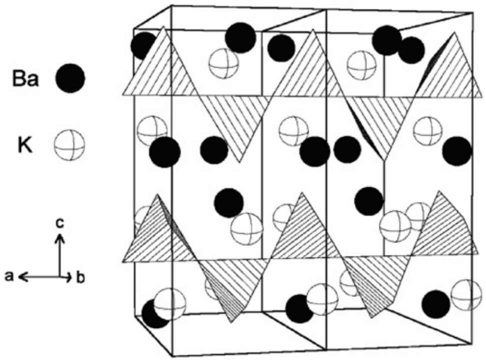

Fig. 1. Structure of $BaKFeO_3$.

pnictide cation and X is an oxygen or nitrogen anion. The M atoms are coordinated by $4X$ atoms to give MX_4 tetrahedra; two of the four corners of each MX_4 tetrahedron is shared with two other MX_4 tetrahedra to give $[MX_3]^{\infty}$ chains.

In $BaKFeO_3$, this leads to Fe^{3+} tetrahedrally coordinated by four oxygen atoms that string together to give anionic $[FeO_3^{3-}]^{\infty}$ chains. The chains are parallel to the *a*-axis and have a periodicity of two tetrahedral units. Both Ba^{2+} and K^+ cations have distorted pentagonal bipyramidal coordination and lie between the chains, isolating them from one another.

The coordination environment for Fe1, shown in Fig. 2, is moderately distorted from ideal tetrahedral symmetry with O–Fe–O bond angles (Table 3) ranging from 101.5° to 112.9°. The Fe–O3 distances bonds within the chain are 1.873 Å, slightly longer than the average Fe–O bond distance of 1.868 Å found for terminal oxygens O1 and O2. Similar lengthening of the bridging bonds is observed not only for all members of the Rb_2TiO_3 structure-type family, but also for the A_3FeO_3 family.

The core of the chain has the structure ⋯O3–Fe1–O3–Fe1⋯ with alternating angles of 101.5° and 152.8 Å for O3–Fe1–O3 and Fe1–O3–Fe1, respectively. The nonlinear Fe–O–Fe bond angle found for $BaKFeO_3$ is in contrast to the linear bridging angles reported for A_3FeO_3-type compounds. Thus the chain found in $BaKFeO_3$ has the same connectivity, but is rather corrugated, compared to the other known ferrate chains.

The relative size of cations A and B appears to have a pronounced influence on the structural chemistry of $ABMX_3$ compounds. For example, all of the known compounds with the Rb_2TiO_3 structure-type are ternary (A and B are the same element). The only exception to this generalization is $BaKFeO_3$, which has unique A and B cations with similar effective ionic radii: Ba^{2+} (1.35 Å) and K^+ (1.38 Å) [20]. Other quaternary candidates for the Rb_2TiO_3 structure-type, such as $RbNaTiO_3$ and $CsNaTiO_3$ [21], have been described, but form chain compounds based on edge-sharing square pyramids. This structure type evidently better accommodates cations with mismatched radii. However, the Rb_2TiO_3 structure type appears to be favored when the radii of A and B are about the same size.

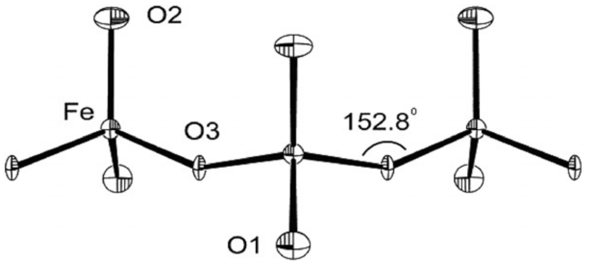

Fig. 2. ORTEP of the $[FeO_3^{3-}]^{\infty}$ chain.

Table 3
Selected bond lengths (Å) and angles (deg) for Fe(1)

Fe(1)–O(1)	1.864 (7)
Fe(1)–O(2)	1.871 (8)
Fe(1)–O(3)	1.873 (2)
O(1)–Fe(1)–O(2)	111.7 (3)
O(1)–Fe(1)–O(3)	108.7 (2)
O(2)–Fe(1)–O(3)	112.9 (2)
O(3)–Fe(1)–O(3)	101.52 (13)
Fe(1)–O(3)–Fe(1)	152.8 (4)

MAPLE calculations [22–25] were performed for $BaKFeO_3$ as a means of checking the plausibility of this new structure. The sums of the calculated partial Madelung energies of the binary compounds BaO, K_2O and Fe_2O_3 agree well with those of $BaKFeO_3$, with a difference of -1.04%. Comparative MAPLE calculations for iron oxides commonly show energy differences of this magnitude [26], which suggests that the energetics of this crystal are in order.

3.3. Magnetism

There is a general interest in Fe(III) chain compounds, as they are isoelectronic with the widely studied Mn(II) low-dimensional magnets [27]. While no magnetic data for the A_3FeO_3 family has been published, low-temperature magnetic data for Cs_2CoO_3 and Rb_2CoO_3 have been reported [17]. These compounds display temperature independent paramagnetism from 300 to 50 K and show a pronounced increase in susceptibility below 50 K. Experimentally determined μ_{eff} values for Cs_2CoO_3 and Rb_2CoO_3 were much lower than expected for a paramagnetic d^5 compound.

We have investigated the low-temperature magnetic behavior of $BaKFeO_3$ and found a gradual increase in molar susceptibility as T approaches 5 K, similar to that observed for Cs_2CoO_3 and Rb_2CoO_3. A plot of molar susceptibility vs. temperature for $BaKFeO_3$ at 10 kG fields is shown in Fig. 3. Data from the lower curve were collected upon heating a sample cooled in zero field; the

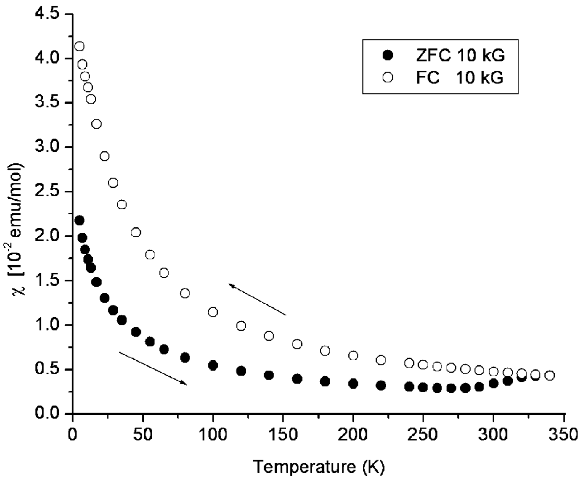

Fig. 3. Zero-field cooled and field-cooled molar susceptibility vs. temperature for $BaKFeO_3$ at 10 kG.

upper curve was collected upon cooling in a field of 10 kG.

The experimentally determined susceptibility values vary greatly depending upon the cooling conditions but in any case are significantly lower than those expected for a high-spin d^5 complex with a spin-only moment of $5.92\,\mu_B$. The attenuated susceptibility can be attributed to antiferromagnetic coupling, which likely occurs along the chain. However, the low-temperature increase in susceptibility cannot be explained by interchain antiferromagnetic coupling, and is likely a consequence of coexisting intrachain ferromagnetic ordering. The observed zero-field cooling effect also supports a model with competing antiferromagnetic and ferromagnetic interactions. Further experiments will be necessary to fully characterize the magnetic properties of this system.

4. Conclusions

In summary, a new quaternary iron oxide, $BaKFeO_3$, has been prepared using a self-sealing molten hydroxide flux technique. The material consists of 1-D chains of corner-sharing FeO_4 tetrahedra that are isolated from one another by barium and potassium cations. A study of the magnetic behavior of $BaKFeO_3$ indicates that the iron spins are coupled to above 350 K.

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