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# Synthesis, structure, and optical properties of a series of quaternary oxides, $K_2Ba(MO_4)_2$ ($M$ = Cr, Mo, W)

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## ABSTRACT

Single crystals of a family of quaternary oxides $K_2Ba(MO_4)_2$ ($M$ = Cr, Mo, W) have been grown for the first time. The crystals were grown in a hydroxide-based hydroflux. The compounds crystallize in space group $R\bar{3}m$ and, according to single-crystal X-ray diffraction structure determination, are isostructural with the mineral Palmierite. All compounds show anti-site mixing of the potassium and barium. The degree of mixing appears to be determined indirectly by the $M$-O bond distance. Diffuse reflectance spectra and room-temperature luminescence were measured for each compound.

## 1. Introduction

Crystal growth of quaternary and higher order oxides is by no means trivial. In order to improve the odds of finding novel compositions with potentially new or improved properties, it is necessary to continuously improve the tools with which the solid state chemist works. For example, molten salts and hydrothermal reactions are staples in the modern toolbox and, historically, alkali metal hydroxides have been a common mineralizer for hydrothermal reactions [1–6]. In the past few decades, many new compositions have been synthesized using molten hydroxide fluxes, particularly, wet hydroxide fluxes or reactions in which water has been purposefully added, to control the acid-base chemistry of the molten flux as described by the Lux–Flood concept of oxo-acidity [7,8].

As more water is added to a hydroxide melt, this wet hydroxide flux will transform into a hydrothermal reaction and vice versa. However, there is a region between the two compositional regimes in which the properties of the reaction media are very much like that of a wet hydroxide flux, but where some of the characteristics of the hydrothermal media are still present. The term hydroflux has been suggested for such a reaction media in which the water content is very high, yet the melting point is above the boiling point of water [9,10].

Palmierite-related oxides have been of interest for a number of properties, including luminescent behavior, ionic conductivity, and ferroelasticity [11–15]. With the focus of many syntheses involving these oxides being the creation of solid solutions to manipulate the electronic and optical properties, it is paramount to have a firm understanding of the crystal structure of the frameworks with which the solid state chemist can tinker.

The series of quaternary oxides, $K_2Ba(MO_4)_2$ ($M$ = Cr, Mo, W), is known, but have only been prepared and characterized as powders previously [16–18]. At one point, $K_2Ba(CrO_4)_2$ was used as a corrosion-resistant pigment and metal alloy primer [19–21], while $K_2Ba(MoO_4)_2$ has been studied as a host for luminescent rare earth ions for lighting applications [11,22–24]. Rare earth doped $K_2Ba(WO_4)_2$ was also recently investigated for its luminescent properties. The fact that all appear to have only been prepared as polycrystalline powders to date, but were readily obtained as single crystals from a hydroflux, highlights the effectiveness of the low temperature hydroflux approach for opening up reaction pathways to complex oxides.

In this paper, we report a new pathway for the synthesis and the first structural characterization by single-crystal X-ray diffraction of this series of quaternary oxides. Optical properties of the materials are determined and compared to relevant oxides.

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**Table 1**
Crystal structure and refinement data for $K_2Ba(MO_4)_2$ ($M$ = Cr, Mo, W).

| Compound | $K_2Ba(CrO_4)_2$ | $K_2Ba(MoO_4)_2$ | $K_2Ba(WO_4)_2$ |
|---|---|---|---|
| Formula weight | 447.54 | 535.42 | 711.24 |
| Color and habit | Yellow prism | Colorless prism | Colorless prism |
| Space group | $R\bar{3}m$ | $R\bar{3}m$ | $R\bar{3}m$ |
| $Z$ | 3 | 3 | 3 |
| $a$ (Å) | 5.7826(16) | 5.9505(4) | 5.9876(3) |
| $c$ (Å) | 21.510(12) | 21.150(3) | 21.075(3) |
| $V$ (Å$^3$) | 611.3(4) | 648.57(12) | 654.34(9) |
| $\rho_c$ (g cm$^{-3}$) | 3.647 | 4.113 | 5.415 |
| $\mu$ (mm$^{-1}$) | 8.426 | 8.331 | 31.731 |
| $F$(000) | 618 | 726 | 918 |
| Crystal size (mm) | 0.05 × 0.05 × 0.01 | 0.53 × 0.20 × 0.20 | 0.10 × 0.08 × 0.08 |
| $\theta_{max}$ (°) | 28.44 | 31.66 | 31.48 |
| Index ranges | $-7 \le h \le 7$;<br>$-7 \le k \le 7$;<br>$-28 \le l \le 28$ | $-8 \le h \le 8$;<br>$-8 \le k \le 8$;<br>$-31 \le l \le 31$ | $-8 \le h \le 8$;<br>$-8 \le k \le 8$;<br>$-30 \le l \le 30$ |
| Reflections collected | 1876 | 2520 | 3616 |
| Independent reflections | 217 | 307 | 309 |
| Goodness-of-fit on $F^2$ | 1.354 | 1.252 | 1.246 |
| $R$ indices (all data) | $R1 = 0.0290$,<br>$wR2 = 0.0633$ | $R1 = 0.0369$,<br>$wR2 = 0.0659$ | $R1 = 0.0200$,<br>$wR2 = 0.0449$ |
| Largest difference peak/hole (e Å$^{-3}$) | 0.559/−0.728 | 0.846/−1.226 | 1.104/−1.163 |

For all structures, $T$ = 298(2) K and $\lambda$ = 0.71073 Å.

## 2. Experimental details

### 2.1. Crystal growth

Crystals of the title series were grown using hydroxide-based hydrofluxes. Reactions were carried out in PTFE-lined, 23 mL Parr autoclaves. The hydroflux consisted of 11 g of KOH (Fisher, certified ACS pellets) and approximately 6 g of distilled water for $K_2Ba(CrO_4)_2$ and $K_2Ba(MoO_4)_2$. For $K_2Ba(WO_4)_2$, a hydroflux composed of 5.5 g of KOH and 3.9 g of NaOH (Fisher, certified ACS pellets) and 6 g of water were employed. Stoichiometric quantities of metal precursors were added to the hydrofluxes. The binary oxides, $MoO_3$ (Alfa Aesar 99.95%) and $WO_3$ (Alfa Aesar 99.9%), and the complex oxide $K_2CrO_4$ (Alfa Aesar, 99% min) were used as the molybdenum, tungsten, and chromium precursors, respectively. During the reaction, the autoclave was sealed to prevent water loss that would otherwise raise the melting point and increase the difficulty of flux removal. The reactions were heated to 230 °C at a rate of 5 °C/min, held for 12 h, and then cooled at a rate of 0.3 °C/min to 60 °C. Single crystals were isolated by decanting the still-molten hydroflux and rinsing the remaining portion with methanol, followed by sonication of the product.

**Table 2**
Atomic coordinates and equivalent isotropic displacement parameters for $K_2Ba(MO_4)_2$ ($M$ = Cr, Mo, W). $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

| | $x$ | $y$ | $z$ | $U_{eq}$ | Occupancy |
|---|---|---|---|---|---|
| $K_2Ba(CrO_4)_2$ | | | | | |
| Ba(1) | 0 | 0 | 0 | 0.0221(4) | 0.825(7) |
| K(1) | 0 | 0 | 0 | 0.0221(4) | 0.175(7) |
| Ba(2) | 0.6667 | 0.3333 | 0.13119(7) | 0.0216(7) | 0.087(3) |
| K(2) | 0.6667 | 0.3333 | 0.13119(7) | 0.0216(7) | 0.913(3) |
| Cr | 0.3333 | 0.6667 | 0.07275(6) | 0.0154(5) | 1 |
| O(1) | 0.1762(4) | 0.3523(8) | 0.09786(16) | 0.0233(10) | 1 |
| O(2) | 0.3333 | 0.6667 | −0.0037(3) | 0.041(2) | 1 |
| $K_2Ba(MoO_4)_2$ | | | | | |
| Ba(1) | 0 | 0 | 0 | 0.0290(4) | 0.775(3) |
| K(1) | 0 | 0 | 0 | 0.0290(4) | 0.225(3) |
| Ba(2) | 0.6667 | 0.3333 | 0.13573(6) | 0.0228(4) | 0.1122(17) |
| K(2) | 0.6667 | 0.3333 | 0.13573(6) | 0.0228(4) | 0.8878(17) |
| Mo | 0.3333 | 0.6667 | 0.07056(3) | 0.0172(3) | 1 |
| O(1) | 0.1731(4) | 0.3463(9) | 0.09801(19) | 0.0320(10) | 1 |
| O(2) | 0.3333 | 0.6667 | −0.0111(3) | 0.054(3) | 1 |
| $K_2Ba(WO_4)_2$ | | | | | |
| Ba(1) | 0 | 0 | 0 | 0.0236(4) | 0.545(6) |
| K(1) | 0 | 0 | 0 | 0.0236(4) | 0.455(6) |
| Ba(2) | 0.6667 | 0.3333 | 0.13611(7) | 0.0183(4) | 0.228(3) |
| K(2) | 0.6667 | 0.3333 | 0.13611(7) | 0.0183(4) | 0.772(3) |
| W | 0.3333 | 0.6667 | 0.070671(19) | 0.01259(17) | 1 |
| O(1) | 0.1735(4) | 0.3471(10) | 0.0983(2) | 0.0257(11) | 1 |
| O(2) | 0.3333 | 0.6667 | −0.0122(3) | 0.048(3) | 1 |

**Table 3**
Selected interatomic distances (Å) and angles (°) for $K_2Ba(MO_4)_2$ ($M$ = Cr, Mo, W).

| | $K_2Ba(CrO_4)_2$ | $K_2Ba(MoO_4)_2$ | $K_2Ba(WO_4)_2$ |
|---|---|---|---|
| Ba(1)/K(1)–O(1) | 2.738(4) ×6 | 2.735(4) ×6 | 2.744(5) ×6 |
| O(1)–Ba(1)/K(1)–O(1) | 67.13(13) | 68.81(14) | 69.21(16) |
| Ba(2)/K(2)–O(2) | 2.741(7) | 2.637(7) | 2.612(10) |
| Ba(2)/K(2)–O(1) | 2.842(4) ×3 | 2.761(4) ×3 | 2.754(5) ×3 |
| Ba(2)/K(2)–O(1) | 2.9635(12) ×6 | 3.0811(11) ×6 | 3.0988(13) ×6 |
| $M$–O(2) | 1.645(7) | 1.726(7) | 1.746(10) |
| $M$–O(1) | 1.651(4) ×3 | 1.750(4) ×3 | 1.757(5) ×3 |

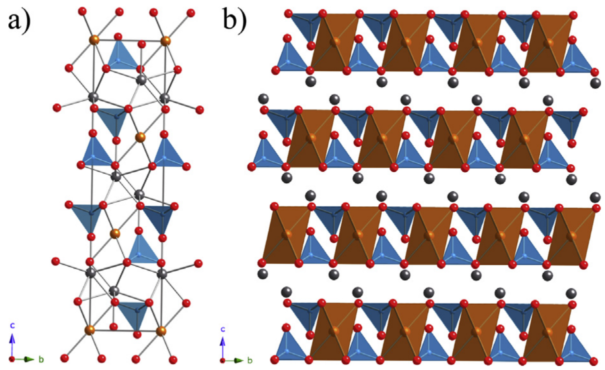

**Fig. 1.** a) Unit cell of the $K_2Ba(MO_4)_2$ structure. Ba atomic sites are shown in orange, K sites in gray, oxygen atoms in red, and $MO_4$ tetrahedra are represented in blue. b) extended structure view of the $K_2Ba(MO_4)_2$ structure with Ba sites shown in orange polyhedra and $MO_4$ tetrahedra in blue to emphasize the layering. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

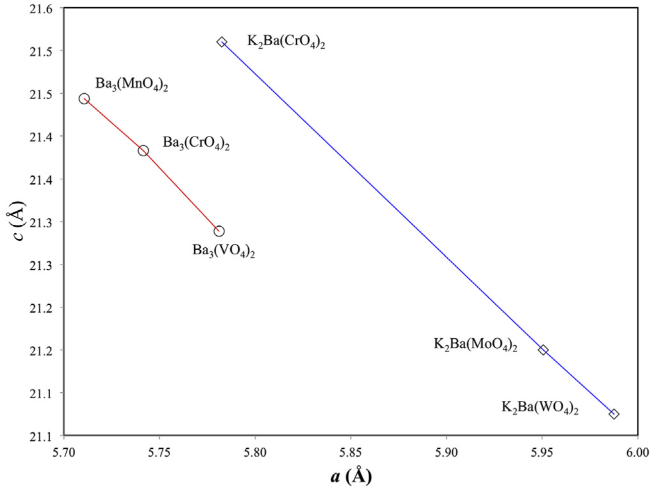

**Fig. 2.** Relation between $c$ and $a$ lattice parameters in the $K_2Ba(MO_4)_2$; $M$ = Cr, Mo, W series and $Ba_3(MO_4)_2$; $M$ = Mn, Cr, V.