Thermo-analytical Investigations on the Superoxides AO_2 (A = K, Rb, Cs), Revealing Facile Access to Sesquioxides A_4O_6

Patrick Merz,^[a] Marcus Schmidt,^[a] Claudia Felser,^[a] and Martin Jansen*^[a,b]

Abstract. Rb_4O_6 and Cs_4O_6 represent open shell p electron systems, featuring charge, spin, orbital and structural degrees of freedom, which makes them unique candidates for studying the ordering processes related, otherwise exclusively encountered in transition metal based materials. Probing the physical responses has been restrained by the intricacy

of synthesizing appropriate amounts of phase pure samples. Tracing the thermal decomposition of respective superoxides has revealed that at least the rubidium and cesium sesquioxides exist in thermodynamic equilibrium, appropriate p-T conditions given. These insights have paved the way to highly efficient and convenient access to Rb₄O₆ and Cs₄O₆.

Introduction

Binary alkali metal oxides constitute an astoundingly diverse body of compounds, displaying plenty of inspiring features. Notably, the full manifold of compositions and structures is based on the alkali metals in the valence state of +1, and thus has rather to be attributed to specific properties of oxygen, e.g. its capability to form polyatomic anions with homoatomic bonds, or, alternatively, to the presence of itinerant excess electrons. The number of individual oxides formed per element grows with the atomic number, and for cesium as many as nine well-defined binary oxides have been reported, cf. pertinent reviews.^[1]

Although synthesis of pure alkali metal oxide compounds, and avoiding contamination during storage and any follow up processing, is posing true challenges, they have achieved significant practical relevance. In solid-state synthesis they are effective ingredients for realizing ternary oxides with e.g. counter-cations in particular coordination arrangements^[2,3] or in less common high or low oxidation states.^[4,5] The first technical application envisaged has been the use of superoxides in air revitalization systems, e.g. for regenerating breathing air in aeronautics.^[6] Quite recently, peroxides and superoxides of Na and Li have attracted considerable attention in the field of electrical energy storage as active components in secondary batteries.^[7] In academic research, open shell oxygen anions, as realized in superoxides (*AO*₂) and ozonides (*AO*₃), have experienced an impressive revival.^[8,9,1e]

Many physical functionalities of materials are based on magnetic exchange interactions resulting from spin and orbital moments of open shell chemical configurations.^[10] In this context, p-electron based magnetism introduces complementary experimental evidences, and different conceptual perspectives, both contributing to a better understanding of the by far pre-

- [a] Max-Planck-Institut f
 ür Chemische Physik fester Stoffe Nöthnitzer Str. 40 01187 Dresden, Germany
- [b] Max-Planck-Institut für Festkörperforschung

vailingly studied d-electron magnetism. Earlier results^[11] obtained on alkali superoxides have recently been broadened substantially, see, for example^[8,9] In particular the so-called alkali metal sesquioxides, Rb_4O_6 and Cs_4O_6 , which feature charge ordering as another degree of freedom, in addition to those related to spin, orbital and structural order-disorder processes, offer rich opportunities for studying entanglement and mutual dependencies of such attributes.^[12]

Unfortunately, dealing with alkali metal oxides experimentally is a demanding undertaking. In particular, when targeting a distinct composition, particular efforts need to be made in controlling the oxygen partial pressure and further relevant synthesis conditions. Exceptions from this rule are the at standard conditions stable forms of the alkali metal oxides Li₂O, Na₂O₂, KO₂, RbO₂, and CsO₂, which can be produced straight forwardly among others by direct combustion of the metals in an excess of oxygen at atmospheric pressure. It is obvious, these well accessible compounds appear to be good starting points for generating further members of this class of compounds with different oxygen contents.

In many cases, existence or non-existence of specific alkali metal oxides with intermediate stoichiometries have been the subject of lasting dissent.^[13] For "Rb₂O₃" or "Cs₂O₃", this controversy has been settled conclusively.^[14,15] Three different synthetic approaches have been suggested, out of which allsolid-state reaction of Rb₂O and RbO₂ in appropriate portions has been reported to be the most reliable with respect to phase purity.^[14] However, performing this recommended synthesis is tedious, in particular it requires to use precisely stoichiometric starting materials, and does not allow to easily produce large amounts as needed e.g. for neutron scattering experiments. Therefore, we have started to look for more convenient synthetic routes, among others considering thermal decomposition of well accessible respective super oxides. Pursuing this goal is meaning to ignore discouraging literature reports explicitly ruling out the formation of any intermediate phase between superoxides and peroxides of rubidium and cesium.^[13c,13e] Because of the static nature of former respective experiments, we regarded it worthwhile to revisit the thermal behavior of the

1

^{*} Prof. Dr. Dr. h.c. M. Jansen

E-Mail: m.jansen@fkf.mpg.de

Heisenbergstr.1

⁷⁰⁵⁶⁹ Stuttgart, Germany

potassium, rubidium and cesium superoxides using state of the art equipment for simultaneous DT and TG analyses.

Results and Discussion

nic and General Chemistry

Zeitschrift für

eine Chemi

We acquired well reproducible and conclusive results. For the rubidium and cesium systems, clear evidence for the existence of intermediate equilibrium phases of composition " A_2O_3 " was obtained, whereas the TGA trace for the potassium superoxide is indicating a transient state of same composition to emerge. These results have pointed the way to an extremely convenient, high yield access to Rb₄O₆ and Cs₄O₆. Most importantly, it has encouraged us to tackle the synthesis of elusive K₄O₆. This has been achieved, though not along simple thermal decomposition of KO₂.^[16]

The mass change of alkali metal superoxides as a function of temperature is shown in Figure 1. The decomposition behavior is characterized by the release of oxygen and the formation of metal-richer solid phases. At temperatures above the given measuring range, uncontrolled mass losses occur due to further thermal decomposition as well as sublimation of the metal formed by disproportionation. Thus, the mass loss can no longer be unambiguously assigned to the formation of a definite product of decomposition. Generally, the occurrence of the individual stages of decomposition is notably more significant in the dynamic vacuum than under the conditions of a flowing argon atmosphere.



Figure 1. Mass change in alkali metal superoxides as a function of temperature in dynamic vacuum and in a flowing argon atmosphere.

The three superoxides investigated exhibit a similar decomposition behavior in the given temperature range. The first step comprises the decomposition of the superoxides to the obviously thermodynamically stable solid equilibrium phase of composition A_4O_6 and oxygen according to the reaction:

$$4AO_2(s) \rightarrow A_4O_6(s) + O_2(g) \ (A = K, Rb, Cs).$$

With increasing temperature, the alkali metal peroxides A_2O_2 form:

$$A_4O_6(s) \rightarrow 2A_2O_2(s) + O_2(g)$$

A further increase in temperature leads finally to complete decomposition into the constituent elements.

As to be expected, the decomposition temperatures of superoxides in dynamic vacuum are generally lower than those in a flowing argon atmosphere. In both cases, the decomposition temperature increases from KO₂ to RbO₂ and CsO₂. For KO₂, a mass loss is already noticeable above 200 °C *in vacuo* and above 340 °C in an argon flow. Thermogravimetry on RbO₂ and CsO₂ reveals a significant mass change above 275 °C in the dynamic vacuum and above 400 °C in flowing argon atmosphere.

Table 1 shows the comparison between theoretical and experimental mass losses (in dynamic vacuum) for the first two thermal decomposition stages. It becomes apparent that the measured mass loss is generally lower than the calculated one. However, with the exception of the value for the second decomposition stage of RbO₂ (6.8% calcd. vs. 4.4% exp.), the deviations lie within the limits of error of 1% to be expected for measurements in a dynamic vacuum. The formation of plateaus for RbO₂ and CsO₂ in the TGA experiments is providing clear evidence that the sesquioxides formed during the first stage of decomposition exist in thermodynamic equilibrium at the p-T conditions prevailing. The relevant parameters like temperature and total pressure obtained are suggesting a straight procedure for synthesizing alkali metal sesquioxides in large amounts. This was demonstrated by decomposing 4 g of CsO₂, and 3.5 g of RbO₂, respectively, in quantitative yield to the respective sesquioxides. Figure 2 displays X-ray powder diffractograms of the obtained single phase Cs_4O_6 , and of Rb₄O₆ containing small amounts of its tetragonal modification,^[12d] the latter is forming slowly at storage at ambient temperature.

Table 1. Calculated and measured relative mass losses during the first and accumulated first and second stage of decomposition for AO_2 (A = K, Rb, Cs).

	Δm /% (calcd.)	Δm /% (measured)
KO ₂ stage 1	11.3	10.2
KO ₂ stage 1+2	22.5	21.1
RbO ₂ stage 1	6.8	6.2
RbO_2 stage 1+2	13.6	10.6
CsO ₂ stage 1	4.9	4.8
CsO_2 stage 1+2	9.7	9.0

Experimental Section

Syntheses: The superoxides AO_2 (A = K, Rb, Cs), were prepared from the respective elements. Potassium was used as purchased (ChemPur, 99,95%), rubidium and cesium were obtained by reducing the respective chlorides with excess calcium according to *Hackspill*.^[17] All handling of the starting materials and products was done in an atmosphere of purified argon. In a typical batch, the respective alkali metal (10 g) was placed into a quartz glass tube, connected to a Schlenk-line. After evacuating the tube, the metal was melted, and dry, purified oxygen was added in small portions. Continuous shaking allowed the metal to remain liquid for a maximum span of time, supporting controlled uptake of oxygen. When no further absorption was noticeable over a period of 1–2 h, the mixture was heated to 100 °C and more oxygen was added in small portions. This procedure was repeated at 150 °C and 200 °C. The resulting product was ground under cooling using a



ic and General Chemistry

Zeitschrift für a

mein<u>e Chemi</u>

Figure 2. Le Bail fits of the X-ray powder diffractograms of as obtained Cs_4O_6 , a = 985.8(1) pm (top), and Rb_4O_6 , two phase refinement, cubic (94%, upper tick marks) a = 932.83(3) pm, tetragonal (6%, lower marks) a = 884.8(1), c = 1028.5(2) pm (bottom).

brass pestle, subsequently annealed under 1 atm of oxygen at 290 °C for two weeks with intermittent grinding, resulting in phase pure samples of the respective superoxides. The as obtained yellow (KO₂, RbO₂), or orange (CsO₂), products were sealed in glass ampoules in an atmosphere of argon.

Cs₄O₆ and Rb₄O₆ were obtained by thermal decomposition of finely ground CsO₂ or RbO₂ (4 g or 3.5 g, respectively) placed in a corundum crucible inside a Schlenk tube, attached to the vacuum line. The superoxides were heated to 290 °C with an approximate heating rate of 100 K·h⁻¹ under dynamic vacuum. While heating, the pressure increased from 2.3 × 10⁻³ mbar to 2.1 × 10⁻² mbar. After 20 h the pressure had dropped to 3.1 × 10⁻³ mbar. In the case of cesium the resulting intermediate was ground again to a fine powder. Repeating heating and subsequent grinding twice for 8 h, each, resulted in black, phase pure powder samples of Cs₄O₆. In case of Rb₄O₆ the decomposition process was repeated only once and was immediately stopped once a sharp pressure drop in the system was noticeable (reaching a range of 10⁻³ mbar). The products were sealed in glass ampoules in an atmosphere of purified argon.

Thermal Analyses: Thermogravimetric investigations were carried out in dynamic vacuum $(1.0 \pm 0.2 \times 10^{-2} \text{ mbar})$ as well as in a flowing

argon atmosphere (Ar 99.999%, 100 mL·min⁻¹, dried, and subjected to oxygen post-purification with a Big Oxygen Trap, Trigon Technologies), using an STA 449 C (Netzsch).

The individual samples were measured under comparable conditions (sample masses: 25–28 mg, rate of heating and cooling: $2 \text{ K} \cdot \text{min}^{-1}$, crucible: corundum with perforated lid, thermocouple: PtRh/Pt). The temperature ranges applied were 25 to 700 °C for KO₂, 25 to 800 °C for RbO₂ and CsO₂ for the measurements in an argon atmosphere, and 25 to 450 °C for KO₂ and RbO₂, 25 to 600 °C for CsO₂ for the vacuum measurements, respectively. The detected mass changes depending on temperature were subjected to buoyancy correction in accordance with the measurement conditions.

Laboratory X-ray Powder Diffraction was performed with an Image Plate Guinierkamera HUBER G670 (Cu- $K_{\alpha 1}$, $\lambda = 0.154056$ nm) at room temperature in the 2θ range 5 to 90° .

Keywords: Alkali metal oxides; Thermal decomposition; Synthesis of alkali metal sesquioxides; Alkali metals

References

- a) N. G. Vannerberg, Prog. Inorg. Chem. 1962, 4, 125; b) I. I. Vol'nov, in Peroxides, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals, (Ed.: A. W. Petrocelli), Plenum Press, New York, 1966, p. 125; c) W. Hesse, M. Jansen, W. Schnick, Prog. Solid State Chem. 1989, 19, 47; d) A. Simon, Coord. Chem. Rev. 1997, 163, 253–270; e) M. Jansen, H. Nuss, Z. Anorg. Allg. Chem. 2007, 1307–1315.
- [2] M. Jansen, Z. Anorg. Allg. Chem. 1982, 491, 175–183.
- [3] a) W. Burow, J. Birx, F. Bernhardt, R. Hoppe, Z. Anorg. Allg. Chem. 1993, 619, 923–933; b) S. Kanungo, B. Yan, P. Merz, C. Felser, M. Jansen, Angew. Chem. 2015, 127, 5507–5510; Angew. Chem. Int. Ed. 2015, 54, 5417–5420.
- [4] a) M. Jansen, R. Hoppe, Z. Anorg. Allg. Chem. 1974, 408, 75–82; b) M. Jansen, R. Hoppe, Z. Anorg. Allg. Chem. 1974, 409, 152–162; c) M. Jansen, Z. Anorg. Allg. Chem. 1975, 417, 35–40.
- [5] a) F. Bernhardt, R. Hoppe, Z. Anorg. Allg. Chem. 1993, 697, 969– 975; b) K. Duriš, U. Müller, M. Jansen, Z. Anorg. Allg. Chem. 2012, 638, 737–743.
- [6] A. W. Petrocelli, A. Capotosto, Aerospace Med. 1964, 35, 440– 443.
- [7] a) T. Ogasawara, A. Débart, M. Holzapfel, P. Novák, P. G. Bruce, J. Am. Chem. Soc. 2006, 128, 1390–1393; b) P. Hartmann, C. L. Bender, J. Sann, A. K. Dürr, M. Jansen, J. Janek, P. Adelhelm, Phys. Chem. Chem. Phys. 2013, 15, 11661–11672.
- [8] S. Riyadi, B. Zhang, R. A. de Groot, A. Caretta, P. H. M. van Loosdrecht, T. T. M. Palstra, G. R. Blake, *Phys. Rev. Lett.* 2012, 108, 217206.
- [9] M. Klanjšek, D. Arčon, A. Sans, P. Adler, M. Jansen, C. Felser, *Phys. Rev. Lett.* 2015, 115, 057205.
- [10] N. A. Spaldin, *Magnetic Materials, Fundamentals and Applications*, Cambridge University Press, Cambridge, **2001**.
- [11] a) M. Rosenfeld, M. Ziegler, W. Känzig, *Helv. Phys. Acta* 1978, 51; b) M. Labhart, D. Raoux, W. Känzig, M. A. Bösch, *Phys. Rev.* B 1979, 20, 53; c) M. Bosch, W. Känzig, *Helv. Phys. Acta* 1975, 48, 743.
- [12] a) J. Winterlik, G. H. Fecher, C. A. Jenkins, C. Felser, C. Mühle, K. Doll, M. Jansen, L. M. Sandratskii, J. Kübler, *Phys. Rev. Lett.* **2009**, *102*, 016401; b) J. Winterlik, G. H. Fecher, C. A. Jenkins, S. Medvedev, C. Felser, J. Kübler, C. Mühle, K. Doll, M. Jansen, T. Palasyuk, I. Trojan, M. I. Eremets, F. Emmerling, *Phys. Rev. B* **2009**, *79*, 214410; c) D. Arčon, K. Anderle, M. Klanjšek, A. Sans, C. Mühle, P. Adler, W. Schnelle, M. Jansen, C. Felser, *Phys. Rev.*

B **2013**, 88, 224409; d) A. Sans, J. Nuss, G. H. Fecher, C. Mühle, C. Felser, M. Jansen, *Z. Anorg. Allg. Chem.* **2014**, 640, 1239.

- [13] a) C. A. Kraus, E. F. Parmenter, J. Am. Chem. Soc. 1934, 56, 2384–2388; b) P. A. Giguere, K. B. Harvey, J. Am. Chem. Soc. 1954, 76, 5891; c) A. Petrocelli, D. L. Kraus, J. Phys. Chem. 1962, 66, 1225; d) A. W. Petrocelli, D. L. Kraus, J. Chem. Educ. 1963, 40, 146; e) S. P. Berardinelli, D. L. Kraus, Inorg. Chem. 1974, 13, 189–191.
- [14] M. Jansen, N. Korber, Z. Anorg. Allg. Chem. 1991, 598/599, 163– 173.
- [15] M. Jansen, R. M. Hagenmayer, N. Korber, C. R. Acad. Sci. Ser. II C 2 1999, 591–594.
- [16] M. Jansen, P.Merz, C.Felser, unpublished results.
- [17] I. Hackspill, Helv. Chim. Acta 1928, 11, 1008.

Received: January 17, 2017

Journal of Inorganic and General Chemistry ZAAC Zeitschrift für anorganische und allgemeine Chemie

P. Merz, M. Schmidt, C. Felser, M. Jansen* 1-5

Thermo-analytical Investigations on the Superoxides AO_2 (A = K, Rb, Cs), Revealing Facile Access to Sesquioxides A_4O_6

