A comparative study of lithium and sodium insertion into $HfMo_2O_8$ and two polymorphs of $ZrMo_2O_8$

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Abstract

Lithium and sodium insertion into RMo_2O_8 (R=Zr,Hf) has been studied by galvanostatic chronopotentiometry, cyclic voltammetry (CV) and quantitative XRD phase analysis as well as by flame photometry after treatment with *n*-butyllithium or sodium naphtalide solutions. Low-temperature modification of $ZrMo_2O_8$ with monoclinic framework structure accommodates two lithiums, in agreement with the topological analysis based on the Voronoi tessellation, at a constant open-circuit voltage of 2.4 V and discharge voltage of ca. 2.1 V. According to CV, the process is partially reversible, but lithium extraction is kinetically hindered, presumably due to the low electronic conductivity of the oxidized phase. Further lithium insertion results in complete amorphization at 4Li per formula unit. This value is limiting also for the isostructural trigonal layered phases, $HfMo_2O_8$ and high-temperature $ZrMo_2O_8$; in those cases, however, amorphization starts from the beginning of reduction. Sodium insertion (both electrochemical and chemical) in the three phases is sterically hindered and could only be detected by CV.
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1. Introduction

Alkali insertion into solid matrices is promising not only for the development of energy storage devices but also for general solid-state chemistry since it allows preparation of new unusual phases which cannot be synthesized directly. In order to understand the principles of these processes and the composition–structure–property relations, we suggest a comparison between isostructural phases with different compositions, between different structures with identical composition (polymorphs), as well as between electrochemical and chemical insertion, between lithium and sodium, etc.

The results of electrochemical lithium insertion into the high-temperature layered form of $ZrMo_2O_8$ have been reported previously [1]. Since that, the compositions RMo_2O_8 (R=Zr, Hf) have received much attention, and several new polymorphs

have been discovered and studied [2–10]. Most of them are high-pressure phases metastable at normal pressure [2–6,10], and even those prepared at normal pressure [7–10] are thermodynamically unstable under ambient conditions. These exotic phases are not considered here; we concentrate only on phases that might be prepared by conventional solid-state reactions: the low-temperature form of $ZrMo_2O_8$ (LZM) and the only stable phase of $HfMo_2O_8$ (HM). Some new evidence on the quenched high-temperature form of $ZrMo_2O_8$ (HZM) will also be reported.

Isostructural HM [8] and HZM [8,11,12] are layered, built of RO_6 octahedra and MoO_4 tetrahedra sharing vertices (Fig. 1a). In LZM [13], the coordination numbers and connectivity are larger: it represents a 3D framework built of distorted ZrO_8 antiprisms and dimeric Mo_2O_8 groups consisting each of two edge-sharing quadrangular pyramids (Fig. 1b). The isostructural $HfMo_2O_8$ could only be prepared at high pressure [6].

In Fig. 1a, pseudo-translations $c'=c/2$ and $a'=a/\sqrt{3}$ are evident. On heating to 190 and 214 °C, respectively, both HM and quenched HZM undergo a displacive phase transition into a higher-symmetry structure in which the above pseudo-translations become the true cell dimensions [8]; obviously, these

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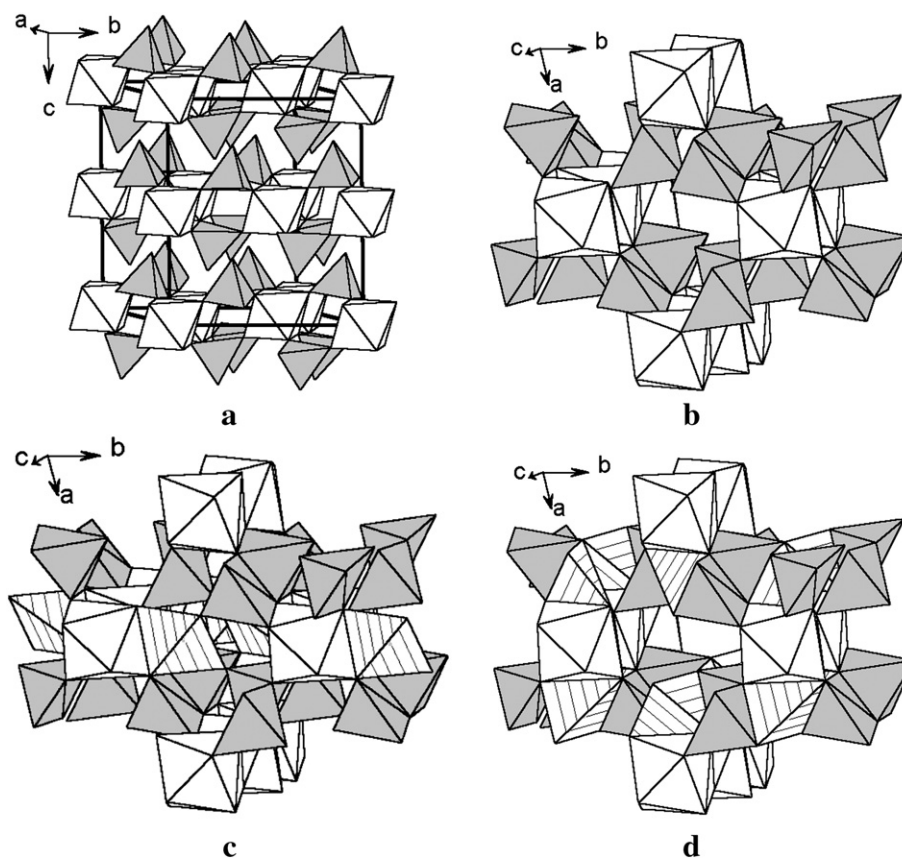*E-mail address:* vbn@rsu.ru (V.B. Nalbandyan).

Fig. 1. Polyhedral presentation of crystal structures. (a) $HfMo_2O_8$ and high-temperature $ZrMo_2O_8$, P-31c [8,11,12]. (b) low-temperature $ZrMo_2O_8$, C2/c [13]. (c) hypothetical $LiZrMo_2O_8$, C2/c. (d) hypothetical $Li_2ZrMo_2O_8$, C2/c. Molybdenum polyhedra, grey; zirconium/hafnium polyhedra, white; lithium tetrahedra, hatched.

intermediate-temperature phases cannot be quenched to room temperature.

2. Experimental

Starting materials were zirconium hydroxonitrate ("zirconylnitrate") analyzed by weight loss on calcination, HfO_2 and MoO_3, all of reagent grade. The reagents were ground together, pressed and calcined for 8 h at 700 °C with intermediate regrindings to obtain HZM and HM. An empirically chosen excess of MoO_3 was taken to compensate for the volatility. A portion of HZM was then annealed for 10 h at 620 °C to produce LZM (note that its direct synthesis from oxides required 3 months at 650 °C [10]). Phase purity of all the products was confirmed by X-ray diffraction.

AC bridge measurements on sintered pellets showed that the three materials were all insulators. Their room-temperature conductivities, too low to be measured directly, were estimated by extrapolation from the Arrhenius plots to be of the order of 10^{-12}–10^{-10} S/cm. To provide a conductivity necessary for electrochemical experiments, 10 wt.% carbon black was admixed, and the mixture was pressed onto a nickel or titanium sample holder. Another electrode was lithium or sodium metal, and a 1 mol/l solution of the corresponding perchlorate in propylencarbonate served as an electrolyte. Electrochemical experiments included cyclic voltammetry (CV) and galvanostatic chronopotentiometry using a P-5848 potentiostat, with periodic X-ray phase analysis (see below).

For chemical insertion, the powdered samples were treated with excess amounts of 1 mol/l solutions of *n*-butyllithium in hexane or sodium naphtalide in tetrahydrofuran (the maximum duration being 10 days), then washed with the corresponding solvent and vacuum-dried. All manipulations with these reagents and alkali metals were performed in a glove box filled with dry argon. The alkali content x per $A_xRMo_2O_8$ formula unit in the chemical insertion was determined by flame photometry, and by the time and current passed in the electrochemical studies.

X-ray analysis was conducted using a DRON-2.0 diffractometer operating in the reflection mode with Ni-filtered $CuK\alpha$ radiation. For the *in situ* studies of electrode reactions, the previously reported technique [1] was used. It is characterized mainly by the two features: (i) a portion of BaF_2 is admixed to the electrode mass as a standard both for the Bragg angle measurements and quantitative phase analysis; (ii) a nickel or titanium sample holder with the electrode mass is tightly covered with a semicylindrical polyethylene lid. This arrangement provides several advantages over flat covers employed usually [14]: the polymer is distant from the goniometer axis and does not produce its own reflections; both incident and diffracted X-ray beams are always normal to the polymer film, thus providing small and equal attenuation at any Bragg angle, which is important for the quantitative analysis; there is enough space for the alkali metal counter-electrode to be placed off the X-ray beam. While horizontal, the sample is covered with the electrolyte solution and electrochemical reactions may proceed.