

SYNTHETIC LITHIOPHORITE : ELECTRON MICROSCOPY AND X-RAY DIFFRACTION

Rudolf GIOVANOLI, Heinz BÜHLER and Krystyna SOKOLOWSKA

Laboratory of Electron Microscopy and Institute of Inorganic Chemistry, University of Berne, 3 Freiestrasse, CH-3000 Berne 9, Switzerland

I. INTRODUCTION

Considerable confusion has been dominating the classification of manganese-oxygen compounds until very recently. The first useful approach was that of de Wolff (8) and Laudy (26) which has initiated several investigations of ourselves (2, 11, 12, 13, 14, 27, 29). The relations between γ -MnO₂ (mineral: nsutite), ramsdellite MnO₂ (no Greek sign attributed), β -MnO₂ (mineral: pyrolusite or polianite), α -MnOOH (mineral: groutite), and γ -MnOOH (mineral: manganite) could thereby be cleared up. The basic structural principle in this group of mineral species are single or double chains of edge sharing octahedra, and intergrowth of these chains. The octahedrally coordinated Mn⁴⁺ ions may also be partly reduced to Mn³⁺ which gives an unlimited number of phases between, e.g., γ -MnO₂ and α -MnOOH.

There are three other groups of poorly crystallized manganese-oxygen compounds left which are distinctly different from the above mentioned group. One is the " δ -MnO₂" (mineral: birnessite); on closer inspection this turned out to be a more complicated compound of analytical composition Na₄Mn₁₁O₂₇·9H₂O, Mn₇O₁₃·5H₂O, and Mn₇O₁₂·6H₂O, depending on the oxidation state of the Mn and on whether or not there are Na⁺ ions present in the lattice (15, 16, 17, 18, 19, 30). It has previously been named "7 Å manganite" (for bibliography see in references 17, 18 and 30); but this is somewhat misleading as there is the mineral species γ -MnOOH named manganite, of entirely different composition and structure. " δ -MnO₂" is misleading either, as the compounds of this group do not belong to the manganese dioxides at all and do not have the composition MnO₂. We have chosen the chemical names sodium manganese(II,III) man-

ganate(IV), manganese(III)manganate(IV), and manganese(II)manganate(IV), respectively*.

A *second group* has first been found in manganese nodules of the oceans by Buser and Grütter (3, 4, 6, 21, 22, 23). It has been synthesized eight years earlier by Feitknecht and Marti and has been named "10 Å manganite" (9, 28). To avoid, again, confusion with manganite (γ -MnOOH), we shall drop this unappropriate name and use the accepted mineral name busserite (after the late Professor W. Buser) for this group. We shall show in another article that the busserite group is a group of hydrates of the above mentioned manganates(IV), differing from these mainly by the layer separation.

A *third group* is the hollandite-cryptomelane group, to which has (incorrectly) been attributed the formula " α -MnO₂"; actually this is a group of non-stoichiometric inclusion compounds of the variable analytical composition Me_{2-x}Mn₈O₁₆ (Me=K⁺, Ba²⁺, Zn²⁺, etc.).

While mainly concerned with the busserite group, our interest has been directed to the lithium aluminium manganese(II)manganate(IV) (mineral: lithiophorite), LiAl₂Mn₂O₉·3H₂O, of which the structure is known from single crystal X-ray data (31). This compound consists of a layer lattice with 10 Å layer separation (1). Since the X-ray powder pattern of the busserite group may also be explained as consisting of a layer lattice with 10 Å layer separation, our interest turned to the synthesis and variability of lithiophorite. The aim was to clarify the difference between the busserite group on the one hand and the hollandite-cryptomelane group on the other hand, and also to show whether there is a true or only a formal relationship between lithiophorite and the busserite group. In other words, the question should be answered: is busserite a group of microcrystalline and non-stoichiometric varieties of lithiophorite with Li⁺ ions replaced by Na⁺ and Al³⁺ by Mn^{2+,3+} or not.

In order to answer this question, lithiophorite was synthesized and investigated in the first place, starting from different cation mixtures. Secondly, we tried to synthesize non-stoichiometric, cation-substituted lithiophorite. It seemed appropriate to us to use primarily the electron microscope, electron diffraction, and X-ray diffraction as tools.

II. EXPERIMENTAL

1. Preparations

In a *first series* of experiments 1 g of mixtures of γ -Al(OH)₃ "Baker's Analyzed" (gibbsite=hydrargillite), Mn₇O₁₃·5H₂O, and LiOH·H₂O "Merck" in varying proportions was enclosed in a folded gold foil (0,2 mm thick) and heated in an auto-

* The IUPAC rules for nomenclature unfortunately do not give decisive indications. They however suggest that endings such as "-ite" should be dropped. For oxide hydroxides they recommend the ending "-ate" where applicable (zincate, aluminate); but otherwise such compounds should be written out as "oxide hydroxide". This would, in the present case, cause considerable confusion with the manganese (III) oxide hydroxides (MnOOH), and we have therefore chosen the above nomenclature.