Substructure and superstructure of four-layer Ca-exchanged birnessite

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Abstract

Synthetic Ca-exchanged birnessite (CaBi) was studied by X-ray and selected-area electron diffraction (XRD, SAED). The substructure of CaBi may be described with a four-layer monoclinic subcell with \( a = 5.150 \), \( b = 2.844 \), \( c = 4c' = 28.16 \) Å, and \( \beta = 90.3^\circ \). Two different superstructures of CaBi were distinguished. CaBi type I has cell parameters \( A = 3a = 15.45 \), \( B = 3b = 8.472 \) Å. The stacking sequence in this unit cell may be described as defect-free OSOS, where successive layers are shifted relative to their predecessors by 0 (O) or \( b/2 \) (S) along the \( a \) axis. The complete description of stacking involves the structure of the layer itself, the structure of the interlayer, and the shift from this layer to the next one. CaBi type II can be described as a regular interstratification of \( A_p = \frac{1}{2}(a - b) \), \( B_p = 4b \), \( \gamma = 118.9^\circ \), and \( A_r = \frac{1}{2}(a + b) \), \( B_r = -4b \), \( \gamma = 118.9^\circ \) supercells that are connected by a mirror plane in projection on the \( a-b \) plane. Its stacking sequence is a random interstratification of OSOS (90%) and OOOOS (10%) structural fragments. Most CaBi crystals appeared to consist of intergrown type I and type II sub-crystals.

As in Na-rich birnessite, the \( A = 3a \) superstructure arises from the ordered distribution of Mn\(^{4+}\)-rich rows parallel to \([010]\) and separated from each other along \([100]\) by two Mn\(^{3+}\) rows. In Mn\(^{4+}\)-rich rows heterovalent Mn cations are regularly distributed according to Mn\(^{4+}\)|Mn\(^{3+}\)|Mn\(^{4+}\) (CaBi type I, \( B = 3b \)) and Mn\(^{3+}\)|Mn\(^{4+}\)|Mn\(^{3+}\)|Mn\(^{4+}\) (CaBi type II, \( B = 4b \)) sequences. Super-periodicities along the \( b \) axis are induced by these regular distributions of heterovalent Mn atoms in Mn\(^{4+}\)-rich rows and of associated interlayer Ca. No significant amount of layer vacancies was detected. Idealized structural formulae for CaBi type I and II are Ca(Mn\(^{3+}\)|Mn\(^{4+}\)|O\(_{18}\) and Ca(Mn\(^{3+}\)|Mn\(^{4+}\))O\(_{24}\), respectively.

Introduction

Buserite and birnessite belong to the family of layered hydrous manganese oxides or phyllomanganates. Their layers are built up of edge-shared Mn-(O,OH)\(_6\) octahedra. The interlayer space between adjacent layers is occupied by exchangeable cations and "H\(_2\)O molecules. Buserite has a 10 Å periodicity along the \( c^* \) axis with exchangeable cations and two layers of H\(_2\)O molecules in its interlayer space. Partial dehydration of 10 Å buserite leads to the formation of 7 Å buserite, which has an interlayer space occupied by exchangeable cations and only one H\(_2\)O layer. Buserite and birnessite occur in a wide variety of geological environments such as marine and oceanic Mn nodules (Burns and Burns 1977, 1978; Chukhrov et al. 1978, 1985, 1989; Glover 1977; Drits et al. 1985), terrestrial and oceanic hydrothermal Mn-rich ore deposits (Chukhrov et al. 1987, 1989; Cronan et al. 1982; Dixon and Skinner 1992; Usui et al. 1989; Usui and Mita 1995), and soils (Taylor et al. 1964; Chukhrov and Gorshkov 1981; Chukhrov et al. 1989; Cornell and Giovanoli 1988).

Because of their unique surface charge, ion-exchange properties, phyllomanganate play an important role in the adsorption and redox processes that occur in various natural environments (McKenzie 1967; Stone and Morgan 1984; Stone and Ulrich 1989; Manceau and Charlet 1992; Stumm 1992; Silvester et al. 1995; Wehrli 1995). To study these cation-exchange properties and the mechanisms of adsorption and redox processes, synthetic buserite and birnessite are used because they are formed easily under laboratory conditions (Bricker 1965; Giovanoli et al. 1970a, 1970b; Murray 1974; Balistrieri and Murray 1982; Strobel et al. 1987; Cornell and Giovanoli 1988) and because they may be considered as synthetic analogs of the natural varieties of these minerals. A comprehensive structural and chemical characterization of these phyllomanganate is required to understand these properties and reaction mechanisms at the atomic scale. However at present the structure and crystal chemistry of buserite and birnessite varieties remain incompletely known. There are only a few studies in which fine structural and chemical properties of natural (Chukhrov et al. 1985, 1989; Manceau et al. 1992; Gorshkov et al. 1992) and synthetic (Post and Veblen 1990; Kuma et al. 1994; Drits et al. 1997; Silvester et al. 1997;