Crystal structure and chemical composition of Li-, Fe-, and Mn-rich micas

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ABSTRACT

The crystal chemistry of three Li-, Fe-, and Mn-rich trioctahedral micas has been characterized by single-crystal X-ray diffraction. The samples are from Hirukawa mine, Japan: (Si3.43Al0.57)(Al1.00Fe0.36Mg0.01Mn0.17Li1.44)(Na0.05K0.95)O10F1.88(OH)0.12; from Mokrusha mine, Russia: (Si3.30Al0.70)(Al1.00Fe0.36Mg0.01Mn0.17Li1.44)(Na0.05K0.95)O10F1.88(OH)0.12; from Sawtooth Mountains, Boise County, Idaho, U.S.A.: (Si1.11Al0.89)(Al1.00Ti0.02Fe0.46Mg0.03Mn0.52Li1.06)(Na0.05K0.92Rb0.02)O10F1.89(OH)0.11. Our crystals belong to the 1Pm3 polytype with layer symmetry C121(1) and show M1 and M3 sites much larger in size than M2. Mean electron-count (m.e.c.) values are more variable for the M1 and M3 sites than for M2. With the exception of the sample from Sawtooth Mountains, all tetrahedral mean bond lengths appear to be smaller for T1 than for T11 site. When compared to the Li- and Fe-rich series, crystals show similar crystal-chemical trends, thus suggesting that the layer structure is affected in a similar way by Fe and Mn cations.

Keywords: Masutomilite, polylithionite, siderophyllite, pegmatite, crystal structure, crystal chemistry

INTRODUCTION

Li-, Fe-, and Mn-rich micas, uncommon in natural environments, are generally characterized by chemical data (Harada et al. 1976; Némec 1983a; Eggleton and Ashley 1989; Menziez and Boggs 1993; Abdalla et al. 1996; Förster et al. 2005). Crystal-structure data are limited or missing. The crystal-structure refinements of holotype masutomilite (Mizota et al. 1986) and norrishite (Tyrna and Guggenheim 1991) represent two relevant exceptions.

Norrishite (KLiMn3Si4O12) is known from one locality (Eggleton and Ashley 1989). It is a trioctahedral oxy-mica where the occurrence of Mn4+ in the octahedral sheet requires the complete deprotonation of the anionic site to match charge-balance constraints (Tyrna and Guggenheim 1991).

Masutomilite (KLiAlMn2+AlSi4O10F2; 0.5 ≤ Mn ≤ 1.0; 3.0 ≤ Si ≤ 3.5; 1.0 ≤ Li ≤ 1.5; 0.5 ≤ Fe ≤ 1.0) is rare but not as unusual as norrishite (Harada et al. 1976; Némec 1983a, 1983b; Mizota et al. 1986). Unlike in norrishite, manganese is divalent and occurs with Fe2+ and Fe3+. This trioctahedral mica shows octahedral ordering that produces a lowering of layer symmetry from the C2/m space group to C2 (Mizota et al. 1986), like in most Li- and Fe-rich micas (cf. Brigatti and Guggenheim 2002 for review of the crystal structure and chemistry of Li-rich micas). More precisely, referring to diperiodic groups (Dornberger-Schiff et al. 1982), the layer symmetry lowers from C12/m1(1) to C121(1), as the result of a different cation ordering in the cis octahedral sites: trivalent cations (mainly Al3+) are ordered at one cis site, whereas Li and Mn occupy the two remaining positions (i.e., the other cis site and the trans site).

Structural data are available for Li- and Fe-rich micas-1M (e.g., Guggenheim and Bailey 1977; Guggenheim 1981; Backhaus 1983; Brigatti et al. 2000). In contrast, no structural data are available for Li-rich micas with Fe and Mn as significant octahedral cations. This paper provides crystal chemical and structural data for three Li-rich micas-1M containing variable, but significant amounts of octahedral Mn and Fe. The aim of this investigation is to clarify the mechanisms of Li and Mn incorporation into the mica layer and to identify the ordering pattern for the octahedral (and possibly tetrahedral) sites.

MATERIALS AND METHODS

Samples

The studied samples are from three well-known localities where mica samples may crystallize as large blades at low pressure and medium temperature in a pegmatite rich in Li and Fe + Mn and in the presence of supercritical vapor, mainly F (Cerny et al. 1985, 1986). At Hirukawa mine (Ena county, Gifu prefecture, Chiba region, Japan, labeled “Hirukawa”) the host rock is a granite with pegmatitic pockets, containing crystals of smoky quartz, orthoclase, topaz, beryl, bertrandite, fluorite, cassiterite, zeolites, rare-earth (REE) minerals, and light yellow to pink micas trending in composition from zinnwaldite to masutomilite (Sueno et al. 2002). The sample studied here is very light pink and consists of several flakes in a star-like textural arrangement.

The Mokrusha mine (Yuzhakova village, Murzinka region, Russia, labeled “Mokrusha”) is at the center of a highly productive granitic pegmatite field (Alabashka field), where large gem-blue topaz, heliodor and aquamarine beryl, smoky quartz, and numerous rare mineral species occur crystallizing on a substrate consisting of albite, microcline, quartz, and muscovite-lepidolite micas (Popov...