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Synthetic hypersilicic Cl-bearing mica in the phlogopite-celadonite join: A multimethodical characterization of the missing link between di- and tri-octahedral micas at high pressures

Sabrina Nazzareni,[1,*] Paola Comodi,[1] Luca Bindi,[2] Oleg G. Safonov,[3] Yuriy A. Litvin,[3] and Leonid L. Perchuk[3,4]

[1]Department of Earth Sciences, University of Perugia, Perugia, Italy
[2]Museo di Storia Naturale, Sezione di Mineralogia, Università di Firenze, Via La Pira 4, I-50121, Firenze, Italy
[3]Institute of Experimental Mineralogy, Chernogolovka, Moscow, Russia
[4]Department of Petrology, Moscow State University, Moscow, Russia

Abstract

A hypersilicic Cl-bearing mica was synthesized at 4 GPa and 1200–1250 °C, close to the solidus of the join diopside-jadeite-KCl, in association with diopside-jadeite pyroxene, K-rich aluminosilicate glass and/or sanidine and (K,Na)Cl. The mica shows a negative correlation between tetrahedral Si and octahedral (Al + Mg), suggesting an Al-celadonitic substitution ($Si + {}^{VI}Al + {}^{VI}\square = {}^{IV}Al + {}^{VI}Mg$) and a chemical formula: $K_{1.01}(Mg_{2.45}Al_{0.19}\square_{0.35})_{\Sigma=3}(Si_{3.52}Al_{0.48})_{\Sigma=4}O_{10}[(OH,O)_{1.66}Cl_{0.34})]_{\Sigma=2}$. The presence of hydroxyl was confirmed by OH stretching modes at 3734 and 3606 cm^{-1} in the Raman spectra. Single-crystal X-ray diffraction data provide the unit-cell parameters (space group *C*2/*m*, 1*M* polytype): a = 5.299(4), b = 9.167(3), c = 10.226(3) Å, β = 100.06(4)°, V = 489.1(4) $Å^3$. The structure refinement shows the presence of vacancies on the octahedral sites (15% for M1 and 6.5% for M2). Chlorine occupies a position about 0.5 Å from O4 with partial occupancy (0.39 apfu). Crystal-chemical mechanisms seem to govern chlorine incorporation in mica, since a large A site is necessary to locate the anion in the structure. A large A site results when the six-tetrahedra ring is hexagonal and the tetrahedral rotation angle α is 0°. Such a geometry is achieved either by increasing the annite component in biotite or by increasing the hypersilicic character of phlogopite through the Al-celadonite substitution. The present Si-rich mica shows a partial dioctahedral character due to the Al-celadonite substitution, which lowers the α angle and expands its stability field at high pressure.

High a_{K_2O} conditions, like in potassium-rich brine or potassic carbonatitic melts, increase the Al-celadonite component in the phlogopite solid solution, explaining the association of Si-rich micas with inclusions of potassic liquids in kimberlitic diamonds.

Keywords: Phlogopite, Al-celadonite, chlorine, high pressure, solid solution, kimberlites, inclusions in diamonds