

# Two synthetic Li-aegirines and their structure analysis

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## Abstract

Two varieties of Li-aegirines in color, green and yellowish green, were formed with a flux process. Both synthetic Li-aegirines crystallize into a monoclinic symmetry with a space group of C2/c. The crystal structure refinements gives the final R factors of 2.1% and 1.9% for the green and the yellowish green Li-aegirine crystals, respectively. On the basis of the results of single-crystal structure refinement, Raman measurement, and chemical composition analysis, the structure features of Li-aegirine were examined.

## Introduction

Pyroxenes (general formula  $M_2M_1Si_2O_6$ ) comprise ~25% of the Earth's volume to a depth of 400 km. A recently discovered phase transformation in Mg-Fe-rich pyroxenes, accompanied by a volume change, is now accepted as an origin of deep-focus earthquakes that cluster at a depth of about 225 km. The structural difference and transition in the pyroxene group have been concerned.

Li-aegirine ( $LiFeSi_2O_6$ ) is a monoclinic, optically biaxial synthetic member of the pyroxene group of minerals and is the homologue to the naturally occurring mineral spodumene  $LiFeSi_2O_6$ . Both compounds belong to the clinopyroxene group and crystallize in space group C2/c at 300K. The room temperature structure of Li-aegirine was first determined by Clark et al. (1969). A study on crystal growth of Li-aegirine synthesized at 1573K and 3 GPa was reported by Redhammer et al. (2001). Recently a series of growth experiment on Li-aegirine with a flux technique at ambient pressure was carried out in the authors' laboratory. The aim of this study is to use a simple synthesis process to crystallize the Li-aegirines and to verify the features of their crystal structure.

## Experimental Procedures

Li-aegirine crystals used in the present study were synthesized by a flux method with  $SiO_2$ - $Li_2CO_3$ - $FeSO_4$  as precursor materials and  $V_2O_5$ - $MoO_3$  as flux substances. Li-aegirine crystals as large as 2mm across can be produced by this technique with a slow cooling process.

Two varieties of flux-grown Li-aegirines in color were found in this work.

Two transparent crystals with well-developed facets, one green and the other yellowish green, were selected for single crystal X-ray diffraction analysis. The X-ray data collection was performed on a Bruker Smart-CCD diffractometer system, and with MoK $\alpha$  radiation ( $\lambda=0.71073 \text{ \AA}$ ). Intensity data were collected in 1271 frames with increasing  $\omega$  ( $0.3^\circ$  per frame), and corrected for  $Lp$  and absorption effects. The unit cell dimensions were determined by a least-squares fit of collected reflections. The crystal structure was analyzed and refined with a full-matrix least-squares method of the Bruker SHELXTAL Version 5.1 system of programs. The crystal structures refinements give the final R factor of 2.1% and 1.9% for the green and yellowish green Li-aegirine crystals, respectively. The chemical compositions of the two were examined with an energy dispersive X-ray spectrometer attached to a JEOL (JSM-840A) scanning electron microscope. Raman spectroscopy measurements were carried out with a Jobin-Yvon Raman spectrometer. A coherent argon ion laser source with a beam of 514.5nm wavelength was employed in this work, and the operation power of the laser was kept at 10mW with the counting time of 100 seconds.

## Results and Discussion

A series of flux-growth runs for Li-aegirine crystals indicate that larger crystals and fewer inclusions of flux components can be formed at slow cooling rates. A number of Li-aegirines crystals with well-developed facets were observed through the growth technique.

The chemical compositions of both samples were determined to be almost pure LiFeSi $_2$ O $_6$ . However, because V $_2$ O $_5$  and MoO $_3$  were added as flux materials in the growth process, trace amount of these components was detected. The small difference of Li-aegirine crystals in color may be attributable to the existence of these impurities.

In Li-aegirine, chains of FeO $_6$  (M1) octahedra separate chains of SiO $_4$  tetrahedra and Li occupies the M2 site. In C2/c symmetry there are three symmetrically non-equivalent oxygens, designated O1, O2, and O3. Observed pyroxene topologies are often characterized by the geometry of their tetrahedral chains and the orientation of those tetrahedral chains relative to their associated octahedral chains. The structural parameter commonly used to describe this geometrical arrangement is the O3-O3-O3 angle. An idealized pyroxene with regular octahedral and tetrahedra and a completely rotated O3-O3-O3 angle of  $120^\circ$  is cubic closest-packed, while an ideal pyroxene with an O3-O3-O3 angle of  $240^\circ$  is hexagonal closest-packed. Real pyroxene can be quite distorted from their ideal equivalent. Both Li-aegirines display the O3-O3-O3 angles of  $181.2^\circ$  and  $181.1^\circ$ ,

respectively, with the tetrahedral chains nearly fully expanded at room temperature. These angles are almost exactly half way between the ideal values of 120° (CCP) and 240° (HCP). These two values are slightly small than those reported previously and thus their structure traditionally has been referred to as S-rotated because the tetrahedral chain with an O3-O3-O3 angle greater than 180°.

Identical to the synthetic Li-aegirine specimen studied by Clark et al. (1969), the cell parameters are  $a=9.672\text{\AA}$ ,  $b=8.667\text{\AA}$ ,  $c=5.299\text{\AA}$ ,  $\beta=110.17^\circ$  for the green one and  $a=9.669\text{\AA}$ ,  $b=8.664\text{\AA}$ ,  $c=5.299\text{\AA}$ ,  $\beta=110.16^\circ$  for the yellowish green crystal. The Li-cation exhibits large anisotropic atomic displacement factors at room temperature with the principal mean square atomic displacement factors  $\langle U^2 \rangle$  being 0.0184, 0.0184, 0.0133  $\text{\AA}^2$  for the green Li-aegirine and 0.01582, 0.02284, 0.1514  $\text{\AA}^2$  for the yellowish green crystal. In contrast to the Ca- and Na-clinopyroxenes, where the M2 site is eightfold-coordinated, the M2 site in Li-aegirine is observed to be 4-coordinated owing to the small Li ionic radius.

Raman analysis also showed that both Raman patterns are very similar to that of Li-aegirine reported by Pommier et al. (2005). The Raman spectra are very similar for  $\text{LiFeSi}_2\text{O}_6$  and  $\text{LiAlSi}_2\text{O}_6$  (spodumene) even though the two materials do not have the same number of Li-O3 bonds. At ambient pressure, the peaks for Li-aegirine are shifted to lower wavenumbers than the same peaks in spodumene. The substitution of iron for aluminum atom changes the M-O bonds and probably also the Si-O bonds.

## References

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