

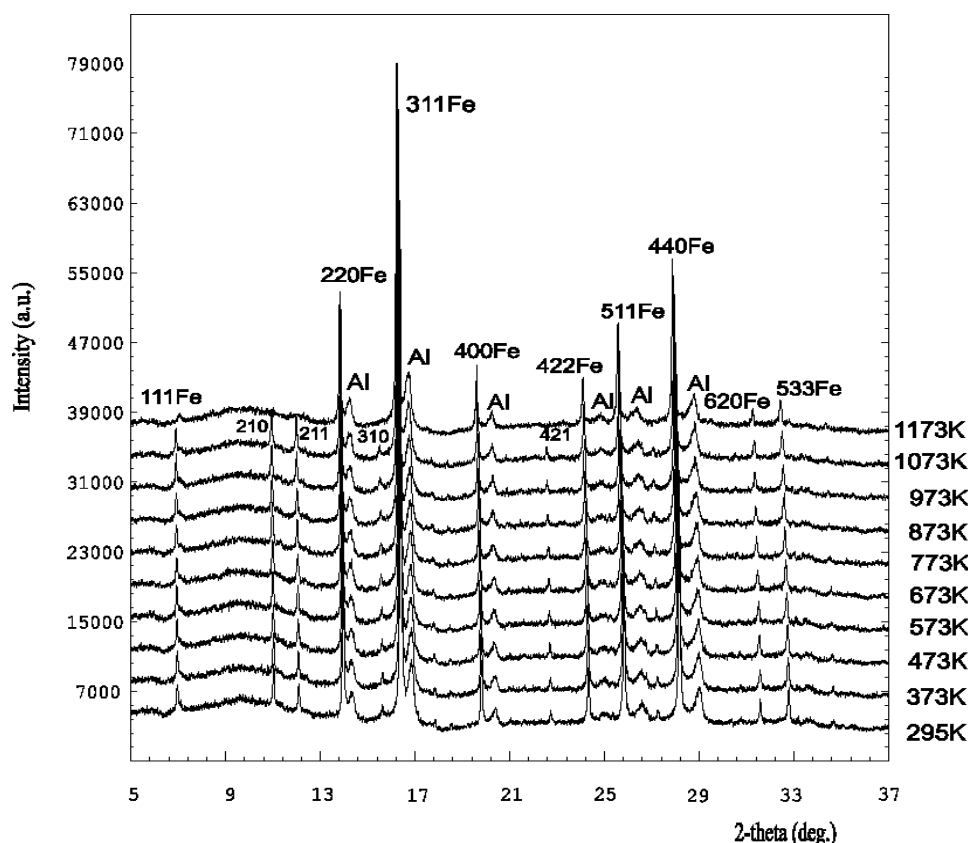
# High Temperature X-ray Powder Diffraction Studies on the $\text{LiFe}_5\text{O}_8$ - $\text{LiAl}_5\text{O}_8$ Spinel Solid Solutions

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Lithium aluminate ( $\text{LiAl}_5\text{O}_8$ ) and lithium ferrite ( $\text{LiFe}_5\text{O}_8$ ) are both inverse spinel oxides, displaying an ordered structure, described as the cubic primitive  $P4_132/P4_332$  space group [1, 2]. Although the end members are isostructural, and the difference in the crystal radii of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  ions is less than 15% [3], the formation of substitutional solid solutions  $\text{LiAl}_y\text{Fe}_{5-y}\text{O}_8$ , *i.e.*, isomorphous replacement of iron by aluminium, is in fact rather limited. In spite of many investigations, data on the concentration limits of solubility are very contradictory. It is known that a miscibility gap is present in the  $\text{LiFe}_5\text{O}_8$ - $\text{LiAl}_5\text{O}_8$  system, and that the phase separation occurs below 1450K [4]. On the other hand, the  $\text{Li}(\text{Fe}_{0.5}\text{Al}_{0.5})_5\text{O}_8$  single-phase solid solution formation, by quenching the sample from 1500K, was reported [5].



**Figure 1:** Synchrotron X-ray powder diffraction patterns recorded during heating of sample with  $\text{LiFe}_{2.5}\text{Al}_{2.5}\text{O}_8$  stoichiometry, in the temperature range 295K-1173K. **Fe** – iron-rich spinel phase ( $\text{LiAl}_y\text{Fe}_{5-y}\text{O}_8$ ); **Al** – aluminium-rich spinel phase ( $\text{LiFe}_y\text{Al}_{5-y}\text{O}_8$ ).

Series of samples with a composition  $\text{LiFe}_{2.5}\text{Al}_{2.5}\text{O}_8$  have been obtained by the solid state reaction of  $\text{Li}_2\text{CO}_3$  with the precursors, composed of a two-phase mixture of the iron-rich and aluminium-rich  $\alpha$ -( $\text{Fe},\text{Al}$ ) $_2\text{O}_3$  solid solutions, by successive thermal treatment at 750°C and 950°C, for 5h, in air. For  $\text{LiAl}_5\text{O}_8$  and  $\text{LiFe}_5\text{O}_8$  preparation the precursors were  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\alpha$ - $\text{Fe}_2\text{O}_3$ , respectively.

For the high temperature experiments the STOE-high-temperature-chamber and the on-site readable Image Plate OBI detector were used at the powder diffraction beamline B2 at HASYLAB/DESY [6]. The wavelength was 0.709901Å. Refinement of diffraction data, collected as a function of  $2\theta$ , and determination of unit cell parameters, was performed using a non-linear least square cell refinement program *UnitCell* [7]. Diffraction patterns presented in Fig.1 exhibit a characteristic doubling of the spinel X-ray lines, revealing the two-phase system. The iron-rich ( $\text{LiAl}_y\text{Fe}_{5-y}\text{O}_8$ ) and aluminium-rich ( $\text{LiFe}_y\text{Al}_{5-y}\text{O}_8$ ) solid solutions coexisted during the thermal treatment up to 1173K, and the formation of single-phase spinel solid solution was not observed. The precise determination of lattice constants of the Fe-rich and Al-rich solid solutions, compared to the unit cell parameters of  $\text{LiFe}_5\text{O}_8$  and  $\text{LiAl}_5\text{O}_8$ , allows to draw a conclusion that differences in the unit cell volume originate in thermal expansion of crystal lattices. The solubility limits, in the temperature range of the present experiment, do not change significantly. Thermal treatment at higher temperature should be indispensable, to solve the problem of single-phase solid solution formation in the  $\text{LiFe}_5\text{O}_8$ - $\text{LiAl}_5\text{O}_8$  system.

**Table 1.** Changes of unit cell parameters of  $\text{LiFe}_5\text{O}_8$ ,  $\text{LiAl}_5\text{O}_8$  and of the Fe-rich and Al-rich  $\text{Li}(\text{Fe},\text{Al})_5\text{O}_8$  solid solutions, during heating from 295K to 1173K.

Temperature (K)	$\text{LiFe}_5\text{O}_8$ $a$ (Å)	$\text{LiAl}_y\text{Fe}_{5-y}\text{O}_8$ Fe-rich phase $a$ (Å)	$\text{LiFe}_y\text{Al}_{5-y}\text{O}_8$ Al-rich phase $a$ (Å)	$\text{LiAl}_5\text{O}_8$ $a$ (Å)
295	$8.3328 \pm 0.0001$	$8.2458 \pm 0.0002$	$7.9963 \pm 0.0003$	$7.9157 \pm 0.0001$
373	$8.3380 \pm 0.0001$	$8.2483 \pm 0.0002$	$7.9905 \pm 0.0003$	$7.9282 \pm 0.0001$
473	$8.3529 \pm 0.0001$	$8.2580 \pm 0.0004$	$8.0128 \pm 0.0003$	$7.9316 \pm 0.0001$
573	$8.3536 \pm 0.0001$	$8.2557 \pm 0.0002$	$8.0080 \pm 0.0002$	$7.9376 \pm 0.0001$
673	$8.3633 \pm 0.0001$	$8.2734 \pm 0.0002$	$8.0141 \pm 0.0002$	$7.9442 \pm 0.0001$
773	$8.3738 \pm 0.0001$	$8.2848 \pm 0.0002$	$8.0163 \pm 0.0002$	$7.9510 \pm 0.0001$
873	$8.3849 \pm 0.0001$	$8.2927 \pm 0.0001$	$8.0247 \pm 0.0002$	$7.9579 \pm 0.0001$
973	$8.3972 \pm 0.0001$	$8.3013 \pm 0.0001$	$8.0353 \pm 0.0001$	$7.9637 \pm 0.0001$
1073	$8.4110 \pm 0.0001$	$8.3115 \pm 0.0003$	$8.0350 \pm 0.0001$	$7.9707 \pm 0.0001$
1173	$8.4252 \pm 0.0001$	$8.3289 \pm 0.0001$	$8.0481 \pm 0.0002$	$7.9805 \pm 0.0001$

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