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Abstract: LiFePO4 has a fully ordered olivine structure in samples prepared by solid state reaction below ~800 °C but, with increasing temperature, a small amount of Li, Fe site exchange occurs reaching a value of about 4% just below melting at 975 °C. The disorder is reversible on annealing at lower temperatures and is detected by changes in lattice parameters and in cation site occupancies obtained by Rietveld refinement of X-Ray Powder Diffraction data.

Thermally-induced cation disorder in $LiFePO_4$

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Abstract

$LiFePO_4$ has a fully ordered olivine structure in samples prepared by solid state reaction below ~800 °C but, with increasing temperature, a small amount of Li, Fe site exchange occurs reaching a value of about 4% just below melting at 975 °C. The disorder is reversible on annealing at lower temperatures and is detected by changes in lattice parameters and in cation site occupancies obtained by Rietveld refinement of X-Ray Powder Diffraction data.

Keywords

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Introduction

Following discovery by Padhi et al[1] that $LiFePO_4$ is able to reversibly deintercalate Li to give the general formula Li_xFePO_4 : $0 \le x \le 1$, and thereby function as a high performance cathode for lithium battery applications, there has been great interest in developing this material as a low-cost and environmentally-acceptable alternative to currently-used Co-based cathodes, principally $LiCoO_2$. For satisfactory cathode performance, the active material must be able to deintercalate rapidly both Li^+ ions and electrons and much attention has focussed on doping $LiFePO_4$ to enhance both its ionic and electronic conductivities. The electronic conductivity is usually enhanced by fabricating composites in which the $LiFePO_4$ grains are coated with a more highly conducting material such as carbon or iron phosphide. Attempts to modify the lithium ion conductivity by doping appear to have been largely unsuccessful.

The olivine structure is built of a hexagonal close packed array of oxide ions containing isolated PO_4 tetrahedra and two energetically distinguishable octahedral sites, M1 and M2. Crystallographic studies have shown in stoichiometric $LiFePO_4$, that Li occupies fully the octahedral M1, 4a site and Fe occupies the octahedral M2, 4c site[2-5]. Cation disorder between the M1, M2 sites is an interesting research area in petrology[6] because it may give insight into the thermal history of the earth's upper mantle where olivine minerals are abundant. In the specific case of $LiFePO_4$, several diffraction studies on materials prepared by low temperature routes have shown a small amount of Li, Fe cation exchange in samples prepared hydrothermally and using wet chemistry[7,8]. A small concentration of Fe on Li sites was visualised in $LiFePO_4$ crystals using dark field scanning transmission electron microscopy, STEM[9]. Above ~180 °C, a fully ordered structure occurred in samples that were prepared hydrothermally as well as by direct solid state reaction.

Li-Fe site exchange, also referred to as the anti-site defect, has been shown to be the most favourable defect in $LiMPO_4$: M=Fe,Mn,Ni,Co by computer simulation[10,11]. This intrinsic defect formation can be represented using Kroger-Vink notation:

$$Li_{Li}^{x} + M_{M}^{x} \rightarrow Li_{M}' + M_{Li}^{\circ} \qquad (1)$$

where ', ^{x} and ^{o} refer to nominal site charges of -1, 0 and +1.

It is not known whether the cation site exchange is an equilibrium feature of the crystal structure of $LiFePO_4$ below 180 °C or is a metastable effect resulting from low temperature synthesis. Antisite disorder has a deleterious effect on electrochemical properties of $LiFePO_4$ since its Li^+ ion mobility is limited to one-dimensional tunnels parallel to [010]; these tunnels are formed by interconnected FeO_6 octahedra and PO_4 tetrahedra, Fig 1. Any immobile Fe^{2+} ions effectively block the channels and reduce the possibilities of Li (de)intercalation[5,7]. In addition to possible antisite disorder, there is also evidence that $LiFePO_4$ can be non-stoichiometric with a small excess of Fe and deficiency of Li in samples given a final heat treatment in N_2 at 725 °C[12].

In this paper, we report a study of the temperature dependence of the crystal structure of $LiFePO_4$ and show that a small amount of cation site exchange occurs under equilibrium conditions at high temperatures which is reversible on subsequent annealing at lower temperature.

Experimental

$LiFePO_4$ powders were synthesised by solid-state reaction. Stoichiometric amounts of Li_2CO_3 (99.99% pure, dried at 180 °C), $NH_4H_2PO_4$ (99.9% pure) and $FeC_2O_4{\bullet}2H_2O$ (99% pure) were weighed out, ground together into a paste with acetone in an agate mortar, dried and placed in a gold foil boat inside a horizontal tube furnace which was hermetically sealed to allow an atmosphere of flowing N_2. The samples were fired initially at 400°C for 3h and 600°C for 3h to decompose oxalates and carbonates, respectively. After cooling to room temperature, samples were reground, pressed to form pellets and heated at higher temperatures for 12h in N_2 using ramps of 5°C/min. After reaction, pellets were crushed and phase purity investigated using a STOE STADI P X-ray powder diffractometer, in transmission mode, Mo Kα_1 radiation (λ=0.7092Å). Indexing of the X-Ray Diffraction, XRD patterns was carried out using WinX^{pow} software. Peak calibration used Si external standard. Structural models were tested by refinement of the XRD data using the General Structure Analysis System, GSAS[13].

Results and discussion

Phase-pure samples of $LiFePO_4$ were synthesised successfully by solid state reaction at temperatures in the range 650 – 800 °C. Heating in N_2 was necessary to avoid oxidation of Fe. Lattice parameter data are summarised in Table 1 for a sample synthesised at 685 °C, reheated at and quenched from 975 °C and then subsequently reannealed at 880 °C. Heating at 975 °C caused an expansion in all three parameters of the orthorhombic unit cell which was largely reversed on subsequent anneal at 880 °C. Literature data for $LiFePO_4$ are also included in Table 1 and are generally similar to those for the samples both synthesised at 685 °C and subsequently annealed at 880 °C.

During the initial stages of Rietveld refinement of XRD data, it appeared that some Li/Fe site exchange had occurred in the sample quenched from 975 °C. Since it is not possible to simultaneously refine site occupancies and thermal parameters of a given site using XRD data, thermal parameters for the Li, Fe sites were obtained first using the 685 °C data set for which there was no evidence of cation site exchange. These parameters were then used, fixed, for all data sets and the Li/Fe cation site occupancies allowed to refine. These thermal parameters were similar to those obtained by refinement of neutron diffraction data[14]. It was assumed that the samples had the stoichiometric $LiFePO_4$ composition and that overall cation site occupancies were full.

Results of Rietveld refinement of X-Ray Powder Diffraction data for the three samples are summarised in Tables 2-4, with a profile plot showing the experimental, calculated and difference profiles for one sample in Fig 2. Satisfactory refinement was obtained for all three samples. It is clear that the sample synthesised at 685 °C had full cation order to within 3esd's, as did the sample that was given a final anneal at 880 °C. However, the sample heated at 975 °C which was found to be just below the melting temperature, showed ~4% anti-site disorder with partial site exchange of Li and Fe between 4a and 4c sites. This amount of cation site exchange is well outside the error range (±3 esds) of the site occupancies, Table 3.

The reversibility of the changes in both lattice parameters and site occupancy with temperature indicates that the cation exchange is an equilibrium process favoured at high temperatures. The lattice parameters of the sample annealed at 880 °C are slightly larger than those of the sample prepared at 685 °C and it is possible, therefore, that the cation order is not complete on reannealing at 880 °C.

The occurrence of significant cation disorder at 975 °C may be understood thermodynamically in terms of the equation $\Delta G=\Delta H-T\Delta S$. The increasing contribution at high temperatures of the $T\Delta S$ entropy component, associated with cation disorder, to the free energy, ΔG, of the sample, acts to offset the unfavourable enthalpy, ΔH, associated with cation site exchange. Thus, difference in size of the Li, Fe^{2+} cations will lead to local structural distortions, as indicated by the increased thermal parameters for oxygen atoms in the sample quenched from 975 °C, Table 3, and therefore, require a positive ΔH value for the cation site exchange.

Such thermally-induced disorder is a common, entropically-driven feature of the crystal structures of many minerals and synthetic compounds. Because of the $T\Delta S$ term, it becomes increasingly important with increasing temperature, as shown by the lattice parameters for the 880 °C sample which are slightly greater than those for the sample prepared at 685 °C but significantly less than those for the sample heated at and quenched from 975 °C.

It is interesting to consider why similar cation disorder to that seen in the present study on quenched, high temperature materials is exhibited in materials synthesised by low temperature routes. It is possible to envisage two scenarios in low temperature synthesis. First, under conditions of thermodynamic equilibrium, low temperature synthesis should give rise to the structure which is most stable thermodynamically and therefore exhibits minimum entropy and maximum order. This appears not to be the case, however when cation site exchange is found in samples prepared by low temperature synthesis[7-9].

Second, under non-equilibrium conditions of materials synthesis, especially by low temperature or chimie douce routes, the first (or an intermediate) product of reaction may represent a state containing high entropy and considerable disorder that, on subsequent treatment may convert to a more fully ordered structure. In this case, the materials synthesised at low temperatures are thermodynamically metastable but kinetically stable. They are able to transform spontaneously to the thermodynamically stable state when they acquire sufficient thermal activation; this, then, accounts for the observation that certain samples prepared by low temperature routes transform to a more ordered structure on heating. The formation of such kinetically-stable but thermodynamically metastable phases as the first product of reaction may represent an example of Ostvald's law of successive reactions[15].

There is considerable structural similarity between the two types of sample exhibiting cation disorder. Those quenched from 975 °C exhibit equilibrium disorder at 975 °C which is preserved in a metastable condition by quenching. Those synthesised by low temperature routes[7-9] are metastable because they represent an intermediate state in the pathway to crystallisation of the fully ordered structure.

There are many examples in the literature of the synthesis of phases that are thermodynamically stable only at high temperatures, but can be either quenched to lower temperature where they are kinetically stable or be synthesised directly at low temperatures where they are kinetically stable although thermodynamically metastable. The only requirement in both cases is that there should be a significant activation barrier for transformation from the metastable to the stable structure. Examples from the authors' laboratory of phases that can be prepared in a metastable state both by quenching from high temperature and by low temperature synthesis include $BaTi_2O_5$[16], α-$Zn_7Sb_2O_{12}$[17], cation-disordered Li_2TiO_3[18] and other rock salt-structured complex oxides exhibiting order-disorder transitions on heating[19]. It appears that $LiFePO_4$, prepared by either low temperature routes or quenching from high temperature and in both cases exhibiting partial cation disorder, also falls into this category.

Finally, there is already significant literature showing that the electrochemical performance of $LiFePO_4$ as a cathode is impaired by cation site disorder in which misplaced Fe^{2+} ions act to block channels for Li (de)intercalation. Samples prepared by high temperature solid state reaction should therefore be given a final anneal at lower temperatures to ensure that cation site disorder is minimised. By contrast, but for the same reason, it is already known that samples synthesised at low temperatures should be given a final anneal at higher temperatures.

Acknowledgements

We thank EPSRC for financial support.

Table 1. Lattice parameters of $LiFePO_4$ after different heat treatments

Heat Treatment	**a/Å**	**b/Å**	**c/Å**	**Volume/Å^3**
Synthesis at 685 °C	10.3287(4)	6.0078(2)	4.6936(2)	291.25
Synthesis at 685 °C followed by heating at 975 °C	10.3535(4)	6.0179(2)	4.7008(2)	292.88
Synthesis at 685 °C followed by heating at 975 and 880 °C	10.3346(2)	6.0102(1)	4.6935(1)	291.52
Ref 5	10.3447(9)	6.0033(5)	4.6964(4)	291.66
Ref 4	10.3377(5)	6.0112(2)	4.6950(2)	291.76

Table 2. Structural parameters of $LiFePO_4$ reacted at 685°C

Atom	**Site**	**x**	**y**	**z**	**Occupancy (%)**	**100×Uiso (Å^2)**
Li	4a	0	0	0	99.4(2)	1.28
Fe	4a	0	0	0	0.6(2)	1.28
Fe	4c	0.2821(1)	0.25	0.9738(4)	99.4(2)	0.46
Li	4c	0.2821(1)	0.25	0.9738(4)	0.6(2)	0.46
P	4c	0.0957(3)	0.25	0.4181(7)	100	1.05(13)
O	4c	0.0940(8)	0.25	0.7479(13)	100	1.98(31)
O	4c	0.4518(9)	0.25	0.2131(10)	100	0.98(24)
O	8d	0.1644(6)	0.0415(8)	0.2800(7)	100	1.06(21)
Space group Pnma, χ^2 =3.91 Rwp=3.96% Rp=3.05%						

Table 3. Structural parameters of $LiFePO_4$ heated at 975°C

Atom	**Site**	**x**	**y**	**z**	**Fraction (%)**	**100×Uiso (Å^2)**
Li	4a	0	0	0	96.3(2)	1.28
Fe	4a	0	0	0	3.7(2)	1.28
Fe	4c	0.2824(1)	0.2500	0.9737(4)	96.3(2)	0.46
Li	4c	0.2824(1)	0.2500	0.9737(4)	3.7(2)	0.46
P	4c	0.0962(3)	0.2500	0.4181(6)	100	1.08(13)
O	4c	0.0954(8)	0.2500	0.7506(13)	100	3.13(33)
O	4c	0.4509(10)	0.2500	0.2162(11)	100	1.49(24)
O	8d	0.1682(6)	0.0386(8)	0.2787(7)	100	1.80(21)
χ^2 =6.02 Rwp=4.69% Rp=3.66%						

Table 4. Structural parameters of $LiFePO_4$ annealed at 880 °C

Atom	**Site**	**x**	**y**	**z**	**Fraction (%)**	**100×Uiso (Å^2)**
Li	4a	0	0	0	99.6(2)	1.28
Fe	4a	0	0	0	0.4(2)	1.28
Fe	4c	0.2821(1)	0.2500	0.9740(1)	99.6(2)	0.46
Li	4c	0.2821(1)	0.2500	0.9740(1)	0.4(2)	0.46
P	4c	0.0951(3)	0.2500	0.4152(6)	100	2.13(14)
O	4c	0.0970(8)	0.2500	0.7441(12)	100	1.92(29)
O	4c	0.4519(9)	0.2500	0.2081(11)	100	1.65(24)
O	8d	0.1651(6)	0.0439(8)	0.2842(7)	100	2.10(21)
χ^2 =5.97 Rwp=4.36% Rp=3.63%						

Figure 1. $LiFePO_4$ structure parallel to (010). Lithium ions are represented as yellow balls and occupy the M1 octahedral site. Iron is octahedrally coordinated in red and green tetrahedra represent the PO_4^{3-} groups.

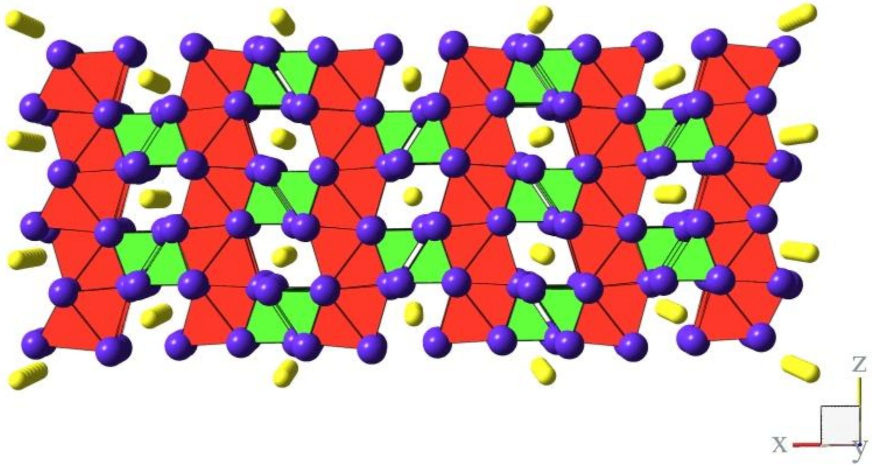
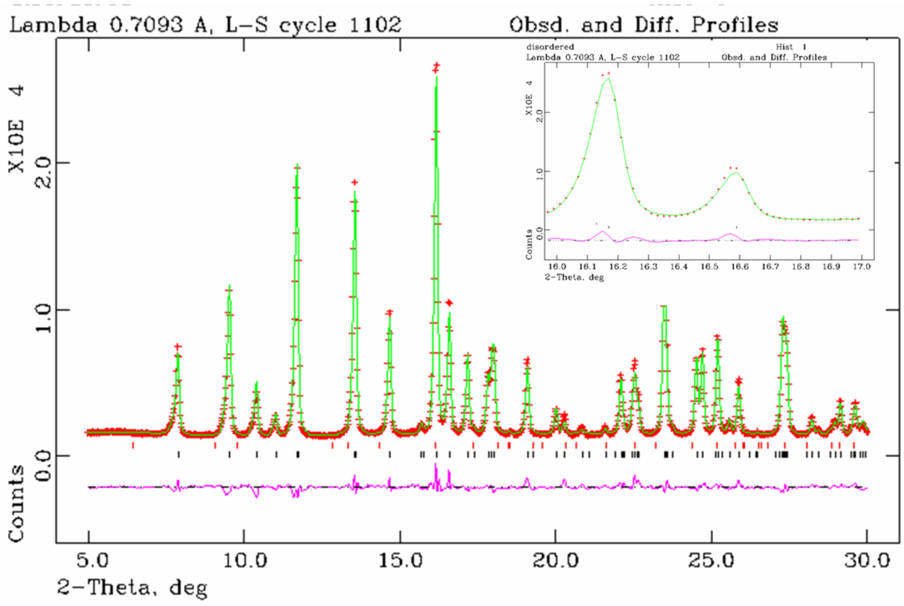


Figure 2. Observed, calculated and difference profile of XRD data for $LiFePO_4$ heated at, and quenched from, 975°C



References

[1] A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *J.Electrochem. Soc.*, 1997, **144**, 1188.

[2] O.V. Yakubovich, M.A. Simonov and N.V. Belov, *Soviet Physics-Doklady* 1977, **22**, 347.

[3] V.A. Streltsov, E.L. Belokoneva, V.G. Tsirelson and N.K. Hansen, *Acta Cryst.* 1993, **B49**, 147.

[4] G. Rousse, J. Rodriguez-Carvajal, S. Patoux, and C. Masquelier, *Chem. Mater.* 2003, **15**, 4082.

[5] J. Chen, M. Vacchio, S. Wang, N. Chernova, P. Zavalij and M.S. Whittingham, *Solid State Ionics*, 2008, **178**, 1676.

[6] S.A.T. Redfern, C.M.B. Henderson, B.J. Wood, R.J. Harrison and K.S. Knight, *Nature*, 1996, **381**, 407.

[7] J. Liu, R. Jiang, X. Wang, T. Huang and A. Yu, *J.Power Sources*, 2009, **194**, 536

[8] S. Yang, Y. Song, P.Y. Zavalij, and M.S. Whittingham, *Electrochem. Comm.*, 2002, **4**, 239

[9] S.-Y Chung, S.-Y Choi, T. Yamamoto and Y. Ikuhara, *Phys. Rev. Lett.*, 2008, **100**, 125502.

[10] G.R. Gardiner and M.S. Islam, *Chem. Mater.*, 2010, **22**, 1242.

[11] C.A.J. Fisher, V.M.H. Prieto and M.S. Islam, *Chem. Mater.*, 2008, **20**, 5907.

[12] P. Axmann, C. Stinner, M. Wohlfahrt-Mehrens, A. Mauger, F. Gendron and C.M. Julien, *Chem. Mater.*, 2009, **21**, 1636.

[13] A.C. Larson, R.B. Von Dreele, Report LA-UR-86-748, Los Alamos National Laboratory, Los Alamos, NM 87545, 1990.

[14] A. Nytén, J.O. Thomas, *Solid State Ionics,* 2006, **177**, 1327.

[15] R.W. Cahn, The Coming of Material Science, 2nd ed, Pergamon Press, Oxford, 2001, pp. 82, 355

[16] N. Zhu and A.R. West, *J Am Ceram Soc*, 2010, **93**, 295-300

[17] G.C. Miles and A.R. West, *J Am Ceram Soc*, 2005, **88**, 396-398

[18] M. Castellanos and A.R. West, J. Mat. Sci., 1979, **14**, 450-454

[19] G.C. Mather, C. Dussarrat, J. Etourneau and A.R. West, *J Mater Chem*, 2000, **10**, 2219-2230

Figure 1

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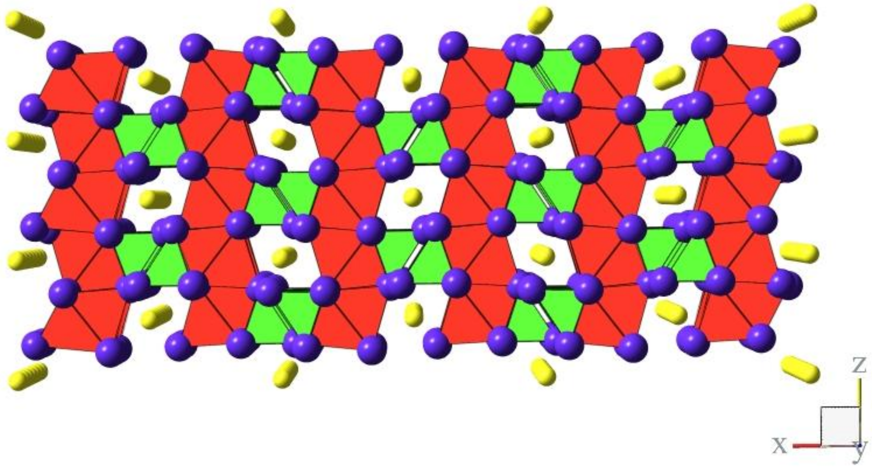
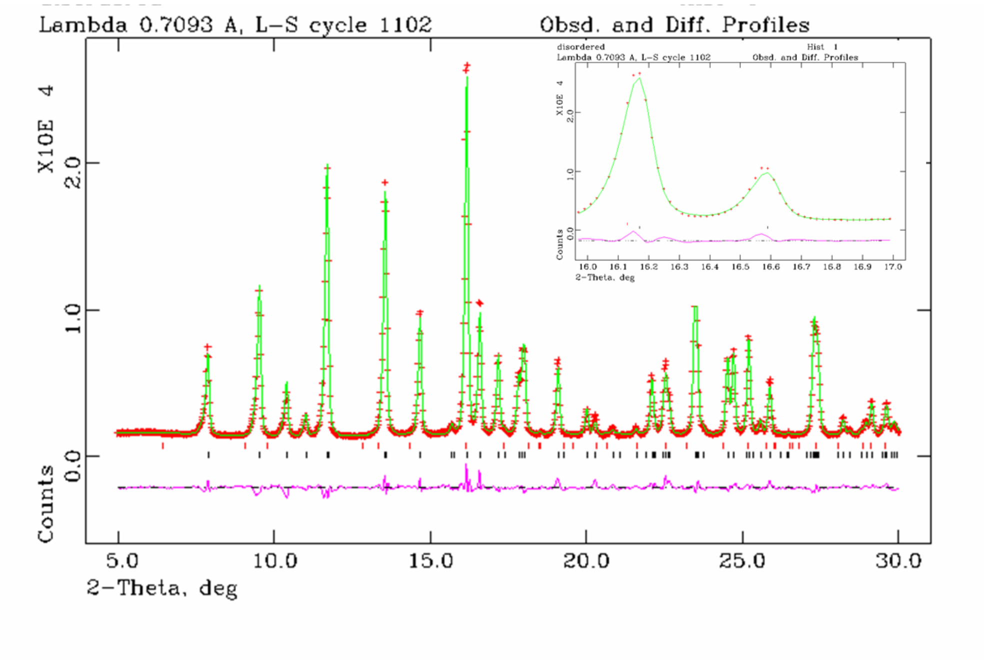


Figure 2

Figure 2. Observed, calculated and difference profile of XRD data for $LiFePO_4$ heated at, and quenched from, 975°C



*Ethical Statement

$LiFePO_4$ is a potential candidate cathode material for next generation lithium batteries. Electrochemical performance depends very much on defect structure. This paper reports temperature dependence of Li/Fe cation mixing and its potential consequences.

***Research Highlights**

$LiFePO_4$ is a potential candidate cathode material for next generation lithium batteries. Electrochemical performance depends very much on defect structure. This paper reports temperature dependence of Li/Fe cation mixing and its potential consequences.