Inorganic Chemistry

Article

pubs.acs.org/IC

$Li_{11}Nd_{18}Fe_4O_{39-\delta}$ Revisited

Peter D. Battle,*[,†] Sian E. Dutton,[‡] Fernande Grandjean,[§,∥] Gary J. Long,[∥] and Katsuyoshi Oh-ishi[⊥]

[†]Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, U. K.

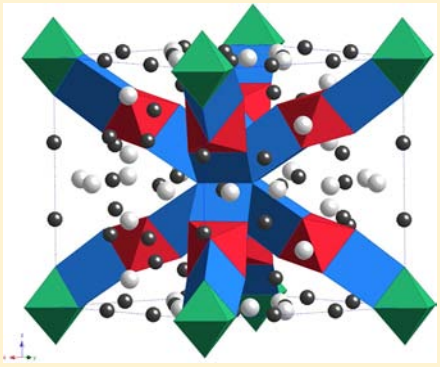
[‡]Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge, CB3 0HE, U. K.

[§]Faculty of Sciences, University of Liège, B-4000 Sart-Tilman, Belgium

[∥]Department of Chemistry, Missouri University of Science and Technology, University of Missouri, Rolla, Missouri 65409-0010, United States

[⊥]Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga Bunkyo-ku, Tokyo 112-8551, Japan

ABSTRACT: The structure proposed for $Li_{11}Nd_{18}Fe_4O_{39-\delta}$ (Chen et al. *Inorg. Chem.* **2012**, *51*, 8073) on the basis of diffraction and Mössbauer spectral data is compared to that determined previously for $Nd_{18}Li_8Fe_5O_{39}$ (Dutton et al. *Inorg. Chem.* **2008** *47*, 11212) using the same techniques. The Mössbauer spectrum reported by Chen et al. has been reinterpreted. The newly refined spectral parameters differ significantly from the published values but are similar to those reported for $Nd_{18}Li_8Fe_5O_{39}$. The relative areas of the three components indicate that iron cations occupy the 2*a*, 8*e*, and 16*i* sites in space group $Pm\bar{3}n$, in disagreement with the model determined from neutron diffraction by Chen et al. in which only the 2*a* and 8*e* sites are so occupied. The relationship between $Li_{11}Nd_{18}Fe_4O_{39-\delta}$ and $Nd_{18}Li_8Fe_5O_{39}$ is discussed, and it is proposed that the sample prepared by Dutton et al. is a kinetic product whereas the sample prepared by Chen et al. is the thermodynamically preferred product.



INTRODUCTION

The crystal structure of $La_{18}Li_8Rh_5O_{39}$, see Figure 1, was deduced from neutron powder diffraction data in 2005.[1] Chains of coordination polyhedra, in which octahedral sites alternate with trigonal prismatic sites, were found to occupy channels within a La−O framework. The chains and channels run along the ⟨111⟩ directions of the cubic unit cell, and the chains intersect each other at (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$). Equivalent octahedral sites are located at these two points of intersection, and a further, crystallographically distinct octahedral site is located halfway between them. The two distinct types of octahedral sites, both occupied by rhodium, are always separated from each other by a prismatic site which is occupied by lithium. The Rh^{3+} and Rh^{4+} cations, which occur in a 4:1 ratio in $La_{18}Li_8Rh_5O_{39}$, are found respectively on the 8*e* and 2*a* sites of space group $Pm\bar{3}n$; the midchain 8*e* site is significantly larger than the 2*a* site at the points of intersection, and the cation ordering is thus consistent with the difference in size of the sites. The Li^+ cations are located on 16*i* sites within the prisms.

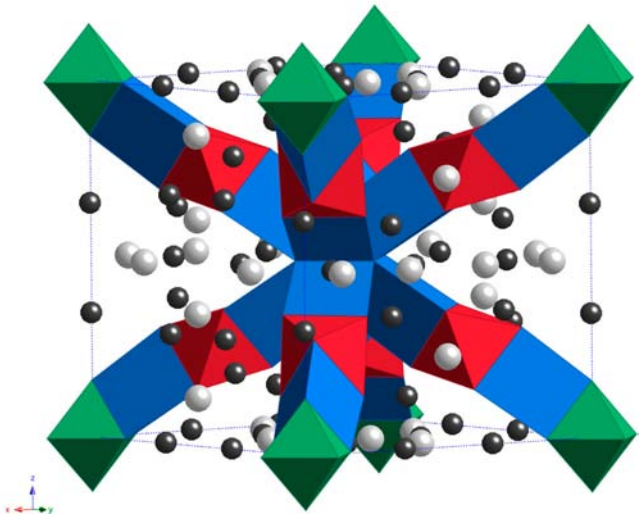


Figure 1. Cubic $La_{18}Li_8Rh_5O_{39}$ structure (space group $Pm\bar{3}n$); gray circles represent oxygen, black circles La. The LiO_6 trigonal prisms are blue (16*i* site), the RhO_6 octahedra are green (2*a* site) and red (8*e*). A 2*a* site at the center of the unit cell is hidden in this view.

Subsequent studies[2−7] have shown that the second-row transition-metal element in $Ln_{18}Li_8Rh_5O_{39}$ (*Ln* = La, Nd, Pr) can be replaced by several combinations of first-row elements to form $Ln_{18}Li_8M_{5-x}M'_xO_{39}$ (*M*, *M*′ = Mn, Fe, Co). Unfortunately, the samples produced have always been contaminated by the excess lithium carbonate used in the synthesis. X-ray diffraction patterns collected on laboratory diffractometers have not always revealed the presence of the impurity phase, but it has been easily identified in neutron

Received: October 3, 2012
Published: January 2, 2013

diffraction patterns. However, the crystal structure of the weakly diamagnetic carbonate is known, and the presence of this second phase has therefore not presented a problem in the analysis of diffraction or magnetometry data collected from these samples.

Recently[8] Chen et al. have carried out a phase-diagram study of the Nd_2O_3–Fe_2O_3–Li_2O ternary system in an attempt to prepare a pure sample for Ln = Nd, $M = M'$ = Fe. They report the synthesis, from a stoichiometric mixture of starting materials, of a monophasic sample of composition $Li_{11}Nd_{18}Fe_4O_{39-\delta}$. Dutton et al. have previously[5] reported the synthesis of $Nd_{18}Li_8Fe_5O_{39}$ contaminated, as usual, by lithium carbonate. X-ray diffraction shows that the two compounds have the same unit-cell parameter. Consequently, Chen et al. suggest that the composition assigned to the compound prepared by Dutton et al. is incorrect. This implies that 20% of the iron in the reaction mixture used by the latter is in a phase other than the principal product. The fact, not commented on by Chen et al., that this material was studied by ^{57}Fe Mössbauer spectroscopy down to 4.2 K without the observation of a second iron-containing phase is therefore surprising, as is the fact that the magnetic susceptibility shows no deviation from paramagnetic behavior above 10 K. The use of a lithium-rich formulation by Chen et al. stems from the analysis of their neutron diffraction data which suggested that 25% of the octahedral 8*e* sites in the structure are occupied by lithium rather than iron cations. Dutton et al. found an Fe:Li ratio of 85:15 on this site, but with the important difference that the prismatic 16*i* site was partially occupied by iron cations so as to maintain the overall composition. This model was consistent with both their neutron diffraction and Mössbauer spectroscopic data. The remainder of the extra lithium required by the composition $Li_{11}Nd_{18}Fe_4O_{39-\delta}$ is attributed by Chen et al. to the partial occupation by lithium of a 24*k* site which was unoccupied in the structural model proposed by Dutton et al. It appears that this additional site lies only 1.57 Å from an oxide ion, and only 1.599 Å from a lithium cation in one of the polyhedral chains. The authors recognize this as an issue and suggest that the two cation sites are not simultaneously occupied, but the implied presence of vacancies on the 16*i* sites and the consequences of this for the composition are not discussed further.

The Mössbauer spectra recorded by Chen et al. do suggest the possible presence of some Fe^{3+} on the 16*i* site in their sample, which would add to the uncertainty in the overall composition. The full-width at half-maximum of this spectral component, 0.194 mm s^{-1}, is as narrow as is permitted by the Heisenberg Uncertainty Principle and is considerably narrower than the other line widths reported by either Chen et al. or Dutton et al. This might be considered surprising in view of the structural disorder around the 16*i* site, although Chen et al. comment that the inclusion of this component was necessary to obtain satisfactory fits. In this paper we report our analysis of the spectrum published by Chen et al.

RESULTS

No further experimental work has been carried out. Rather we have digitized and refitted the experimental data shown in Figure 5 from reference 8. Unfortunately, Chen et al. failed to report[8] the percentage transmission in their Mössbauer spectrum. We have therefore assumed that the percentage transmission was similar to that observed[5] earlier, and we have fixed the minimum transmission at 98%. First, we fitted the experimental data with the spectral parameters constrained to be identical to the published fit parameters given in Table 4 of reference 8; we refined only the baseline and the total spectral absorption area. As expected, this leads to a fit that is virtually identical to that shown in Figure 5 of reference 8. Second, we refined the isomer shift, δ, the quadrupole splitting, ΔE_Q, the full width at half-maximum, Γ, and the percentage area of each of the three doublets, as well as the baseline, and the total absorption area, that is, a total of 14 parameters. This refinement used the highly robust and efficient Levenberg–Marquardt algorithm. The result of this fit is shown in the lower portion of Figure 2; the fit previously reported in reference 5

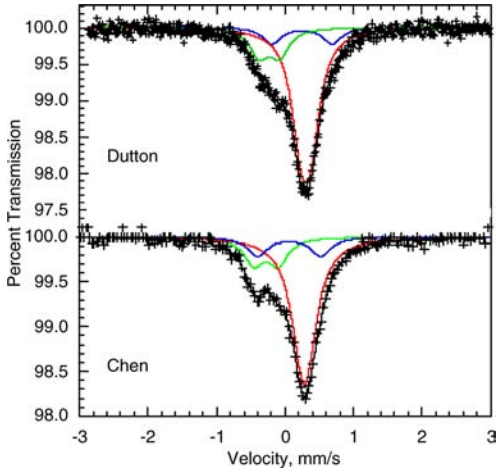


Figure 2. Room temperature Mössbauer spectra of $Nd_{18}Li_8Fe_5O_{39}$ previously published by Dutton, et al. in reference 5, top, and of $Li_{11}Nd_{18}Fe_4O_{39}$ obtained from Chen, et al. in reference 8 and fitted with three unconstrained symmetric quadrupole doublets, bottom. The vertical scale of the lower spectrum is an approximation because no scale is given in reference 8. The colors used to distinguish the three components in this figure correspond to those used for the different sites in Figure 1; the 2*a*, 8*e*, and 16*i* sites are in green, red, and blue, respectively.

for $Nd_{18}Li_8Fe_5O_{39}$ is shown for comparison in the upper portion of this figure. In this refinement, rather surprisingly, we obtained a lower χ^2 value than that obtained in the first step, an indication that the fit shown in Figure 5 of reference 8 is not the best possible fit. More significantly, all the line widths refined to normal values that are similar for the three components. Further, this fit avoids the significant misfitting present at both −0.2 and +0.6 mm/s in Figure 5 of Chen et al.; the misfitting is primarily associated with the artificially narrow line width of the doublet tentatively assigned by them to the 16*i* site. Our refined parameters are given at the bottom of Table 1; the parameters published in references 5 and 8 are given for comparison at the top and center of this table, respectively.

DISCUSSION

It is quite clear that the fit published by Chen et al.[5] for $Li_{11}Nd_{18}Fe_4O_{39}$ had not properly converged. This failure to converge may be a consequence of the extensive correlations between the refined spectral parameters, as is shown by our correlation matrix. Further, the reported spectral parameters were given with more significant figures than is justified by the estimated, but not statistically obtained, accuracies. The refined fit obtained herein for the $Li_{11}Nd_{18}Fe_4O_{39}$ spectrum yields spectral parameters that are very similar to those reported in

dx.doi.org/10.1021/ic302209d | *Inorg. Chem.* 2013, 52, 950–952

Table 1. Mössbauer Spectral Parameters for $Nd_{18}Li_8Fe_5O_{39}$ and $Li_{11}Nd_{18}Fe_4O_{39}$

compound	site	δ,[a] mm/s	ΔE_Q, mm/s	Γ, mm/s	area, %	assignment	ref.
$Nd_{18}Li_8Fe_5O_{39}$[b]	2*a*	−0.229(9)	0.30(2)	0.33(2)	19.99	iron(IV)	5
	8*e*	0.306(1)	0.149(8)	0.332(7)	68.17	iron(III)	5
	16*i*	0.27(1)	0.88(3)	0.33(3)	11.84	iron(III)	5
$Li_{11}Nd_{18}Fe_4O_{39}$[c]	2*a*	−0.296(20)	0.334(20)	0.360(20)	21.8(2.0)	iron(IV)	8
	8*e*	0.294(20)	0.041(20)	0.418(20)	71.6(2.0)	iron(III)	8
	16*i*[d]	0.077(20)	0.948(20)	0.194(20)	6.7(2.0)	iron(III)	8
$Li_{11}Nd_{18}Fe_4O_{39}$[e]	2*a*	−0.28(3)	0.35(5)	0.34(4)	20(5)	iron(IV)	*e*
	8*e*	0.282(4)	0.08(3)	0.38(2)	65(2)	iron(III)	*e*
	16*i*	0.06(3)	0.92(7)	0.35(5)	15(3)	iron(III)	*e*

[a]The isomer shift is given relative to α-iron at room temperature. [b]The relative spectral areas of the three components have been constrained to agree exactly with the iron occupancies obtained from neutron diffraction refinements reported by Dutton et al. in reference 5. [c]The proposed stoichiometry and the Mössbauer spectral parameters reported by Chen et al. in reference 8. [d]This component was assigned by Chen et al. to a partial iron(III) occupancy of the 16*i* site. [e]The best fit refinement obtained herein for the experimental Mössbauer spectral data reported by Chen et al. in Figure 5 of reference 8.

reference 5 for $Nd_{18}Li_8Fe_5O_{39}$. The major difference is the spectral area assigned to the 16*i* site that is larger herein than in reference 5 and accounts for the increased absorption at −0.4 mm/s in the lower spectrum in Figure 2 as compared to the upper spectrum. Consequently, the Mössbauer spectrum published by Chen et al.[8] does not support their neutron diffraction refinement, in which iron cations occupy only the 2*a* and 8*e* sites in a ratio of 1:3. In contrast, the Mössbauer spectrum agrees very well with the iron occupancies of the 2*a*, 8*e*, and 16*i* sites proposed in reference 5 for $Nd_{18}Li_8Fe_5O_{39}$, but with a slightly larger occupancy of the 16*i* sites. Alternatively, the third doublet in blue in the lower spectrum in Figure 2 with a relative area of 15(3) % could be assigned to an undetermined iron-cation containing impurity and then the green and red doublets assigned to the 2*a* and 8*e* sites have an area ratio of 1:3.3 close to the 1:3 expected from the neutron diffraction refinement. In this case, the presence of three doublets in the Mössbauer spectrum certainly does not support the claim of purity of the samples prepared[8] by Chen et al.

There is one further aspect of the model proposed by Chen et al. that should be considered carefully. Although they claim to have prepared monophasic samples, they state that the sample used in their neutron diffraction experiment contained 1.9 wt % $LiFeO_2$. As a result of the large difference in relative molecular mass between the impurity and the principal phase, this corresponds to a molar ratio of ∼1:1.38. The composition of the sample from which the structural model is derived therefore differs significantly from the ideal formulation. Unfortunately, the impurity was not detected in their preliminary X-ray studies. The neutron diffraction pattern shown by Dutton et al. reveals no such impurity, and the Mössbauer spectra they present do not show a component that is consistent with the hyperfine parameters reported previously[9,10] for $LiFeO_2$ or $NdFeO_3$, the two most likely iron-containing impurities. We estimate the detection limit of these spectra to be ≤3%. Furthermore, when Dutton et al. attempted to prepare $Nd_{18}Li_8Co_5O_{39}$ they detected a 2.6 wt % (1:1 molar) $LiCoO_2$ impurity by in-house X-ray diffraction and subsequently prepared a monophasic sample of $Nd_{18}Li_8Co_4O_{39}$. This suggests that the samples of Dutton et al. were subjected to a particularly rigorous check for impurities, and that had 20% of the iron in their reaction mixture been in a second phase it is likely that it would have been identified.

CONCLUSION

Although it is easy to accept that the samples prepared by the two groups have different compositions, it is not obvious that the composition assigned by Dutton et al. to their sample is incorrect. The samples prepared by Chen et al. were heated for 12−24 h at 950 °C, whereas Dutton et al. synthesized their samples by heating at 950 °C for only 1 h. It is thus possible that the sample prepared by Dutton et al. is a kinetic rather than thermodynamic product.

AUTHOR INFORMATION

Corresponding Author

*E-mail: peter.battle@chem.ox.ac.uk.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Frampton, P. P. C.; Battle, P. D.; Ritter, C. *Inorg. Chem.* **2005**, *44*, 7138.
(2) Battle, P. D.; Dutton, S. E.; Thammajak, N.; Grandjean, F.; Sougrati, M. T.; Long, G. J.; Oh-ishi, K.; Nakanishi, S. *Inorg. Chem.* **2010**, *49*, 5912.
(3) Battle, P. D.; Dutton, S. E.; van Daesdonk, P. A. *J. Solid State Chem.* **2010**, *183*, 1620.
(4) Battle, P. D.; Dutton, S. E.; Grandjean, F.; Long, G. J.; Thammajak, N.; Wisetsuwannaphum, S. *J. Solid State Chem.* **2011**, *184*, 2580.
(5) Dutton, S. E.; Battle, P. D.; Grandjean, F.; Long, G. J.; Oh-ishi, K. *Inorg. Chem.* **2008**, *47*, 11212.
(6) Dutton, S. E.; Battle, P. D.; Grandjean, F.; Long, G. J.; van Daesdonk, P. A. *Inorg. Chem.* **2009**, *48*, 1613.
(7) Dutton, S. E.; Battle, P. D.; Grandjean, F.; Long, G. J.; Sougrati, M. T.; van Daesdonk, P. A.; Winstone, E. *J. Solid State Chem.* **2009**, *182*, 1638.
(8) Chen, Y.; Reeves-McLaren, N.; Bingham, P. A.; Forder, S. D.; West, A. R. *Inorg. Chem.* **2012**, *51*, 8073.
(9) Cox, D. E.; Shirane, G.; Flinn, P. A.; Ruby, S. L.; Takei, W. J. *Phys. Rev.* **1963**, *132*, 1547.
(10) Eibschutz, M.; Shtrikman, S.; Treves, D. *Phys. Rev.* **1967**, *156*, 562.