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New solid state exchange reactions of lithium ferrites with $ZnSO_4$

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Heating of a pelletized mixture of $LiFe_5O_8$ and $ZnSO_4$ in air at 650–700 °C results in a solid state exchange (metathesis) reaction with formation of $ZnFe_2O_4$. The rate of reaction is greater if orthoferrite $LiFeO_2$ is used instead of ferrospinel $LiFe_5O_8$. Owing to ready formation of $ZnSO_4$ during thermal dehydration, anhydrous $ZnSO_4$ can be substituted for $ZnSO_4{\cdot}7H_2O$ without substantial effect on the reaction rate.

One of the promising directions in the development of new materials is the synthesis of functionally graded materials, when a spatial gradient of chemical composition results in substantial improvement of functional properties or appearance of new effects.[1,2] Synthesis of these materials often requires application of special methods. One such method might be solid state metathesis (SSM, or chemical exchange) reactions, which while well established, has been attracting growing interest over the last ten years.[3]

One of the critical requirements of SSM process conditions is that the reaction temperature should be close to the temperature of physical or chemical transformation of one of the precursors or reaction products. SSM synthesis is used for preparation of the large number of oxygen-free binary or multicomponent products such as borides,[4] nitrides,[5] pnictides[6] *etc.* One of the few examples of SSM with oxygen-containing species is reaction (1)

$$MnCl_2 + 2LiFeO_2 \rightarrow MnFe_2O_4 + 2LiCl \qquad (1)$$

realized 65 years ago by heating a fine mixture of the precursors at 500 °C.[7]

Taking into account the high chemical reactivity of lithium ferrites, reactions involving these seem also to be probable. A thermodynamic estimate of ΔG for reaction (2)

$$ZnSO_4 + 4Li_{0.5}Fe_{2.5}O_4 \rightarrow ZnFe_2O_4 + Li_2SO_4 + 4Fe_2O_3 \quad (2)$$

is -40 kJ mol^{-1}. This reaction can also be promoted by transformation of $ZnSO_4$ into its high-temperature modification at 700 °C.[8]

To study the possibility of such a reaction, finely powdered lithium orthoferrite $LiFeO_2$ and ferrospinel $Li_{0.5}Fe_{2.5}O_4$ have been prepared using the freeze-drying technique. Anhydrous $ZnSO_4$ was obtained by thermal dehydration of commercial $ZnSO_4{\cdot}7H_2O$. X-Ray diffraction patterns of the mixture, corresponding to the stoichiometry of reaction (2), pelletized and annealed at 700 °C for 1 h, demonstrated complete disappearance of reflections of inverse spinel, belonging to $Li_{0.5}Fe_{2.5}O_4$, and appearance of normal spinel reflections which can be attributed only to $ZnFe_2O_4$.

Unlike most known SSM reactions, where the second product of the reaction can be removed by dissolution in water or other solvents,[3] reaction (2) appears impractical for practical applications owing to the complicated separation of Fe_2O_3 and $ZnFe_2O_4$. This problem can be solved taking into account the ability of Fe_2O_3 to reduce the temperature of $ZnSO_4$ decomposition, which normally occurs at 750 °C.[9] Annealing of a mixture corresponding to reaction (3)

$$5ZnSO_4 + 4Li_{0.5}Fe_{2.5}O_4 \rightarrow 5ZnFe_2O_4 + Li_2SO_4 + 4SO_2 + 2O_2 \qquad (3)$$

at 700 °C resulted in complete consumption of $ZnSO_4$ accompanied by reduction of Fe_2O_3 reflections to the background level (Fig. 1), so that almost single phase $ZnFe_2O_4$ can be obtained upon washing the reaction products. Formation of $ZnFe_2O_4$ is confirmed also by a dramatic reduction of the magnetic response of the reaction mixture due to transformation of ferrimagnetic $Li_{0.5}Fe_{2.5}O_4$ into paramagnetic zinc ferrite.

Analysis of XRD patterns for intermediates of reaction (3) demonstrates some interesting features of the process [Fig. 2(a)]. Initially there are substantial quantities of Fe_2O_3 and ZnO which then disappear (completely, if annealing is accompanied by intermediate grinding) during subsequent thermal treatment. Such behavior may be ascribed to the complex, multistage topochemical mechanism of the metathesis reaction, where the formation of Li_2SO_4 proceeds substantially faster than formation of the other products. XRD monitoring of the reaction products indicates the absence of Li_2SO_4 reflections. However, analysis of washing solutions after ultrasonic treatment of the reaction products in water confirmed the presence of large amounts of SO_4^{2-} ions which appear to be attributable only to Li_2SO_4. No evidence of easily crystallized Li_2CO_3 or other Li-containing species was observed by XRD.

The metathesis reaction of $Li_{0.5}Fe_{2.5}O_4$ with $ZnSO_4$ appears to be facilitated by the similarity of the crystal structures of the initial and product spinel ferrites, though the formation of $ZnFe_2O_4$ from ZnO and Fe_2O_3 is the slowest stage of reaction (3). This fact led us to turn our attention to another lithium

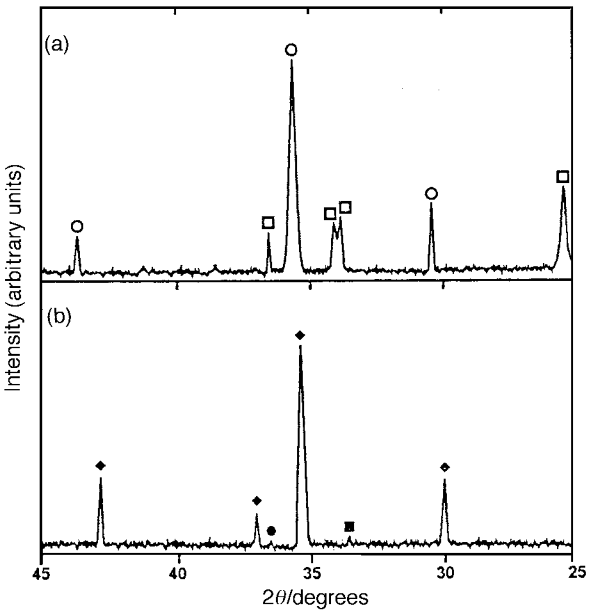

Fig. 1 XRD patterns of precursor mixture and final product of SSM reaction: (a) $4Li_{0.5}Fe_{2.5}O_4 + 5ZnSO_4$; (b) sample (a) after a single firing at 700 °C for 2 h: (□) $ZnSO_4$, (◆) $ZnFe_2O_4$, (○) $Li_{0.5}Fe_{2.5}O_4$, (■) Fe_2O_3, (●) ZnO.

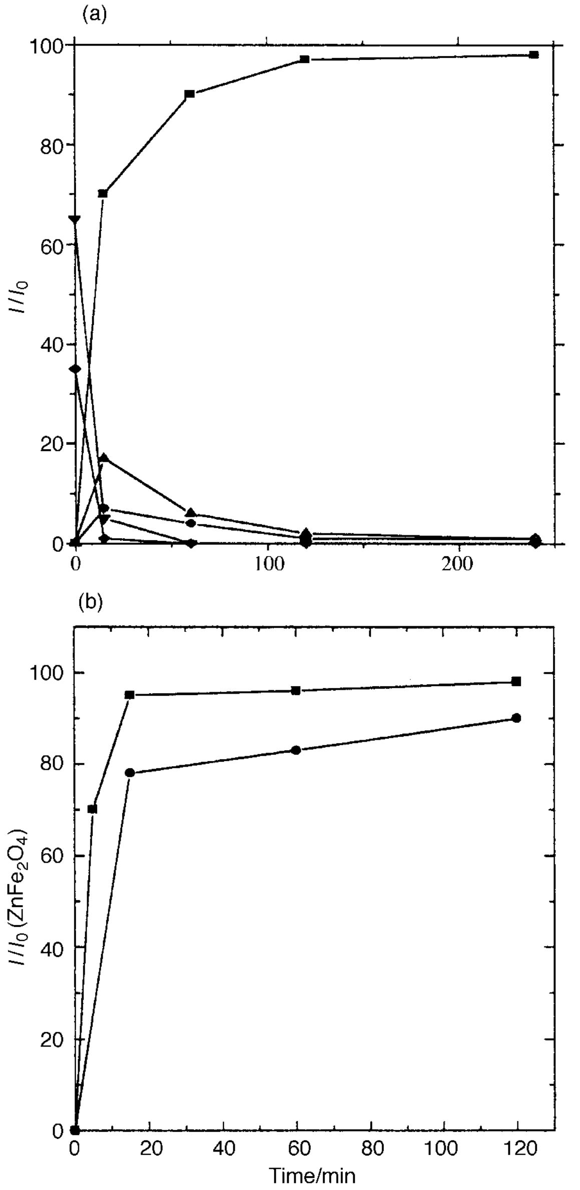

Fig. 2 (a) Dynamics of XRD reflection intensities during calcination of the mixture of $Li_{0.5}Fe_{2.5}O_4$ and $ZnSO_4$ at 700 °C: (■) $ZnFe_2O_4$, (●) ZnO, (▲) Fe_2O_3, (▼) $Li_{0.5}Fe_{2.5}O_4$, (◆) $ZnSO_4$. (b) XRD traces showing $ZnFe_2O_4$ formation from $LiFeO_2$ and $ZnSO_4$ at 650 °C (●) and 700 °C (■).

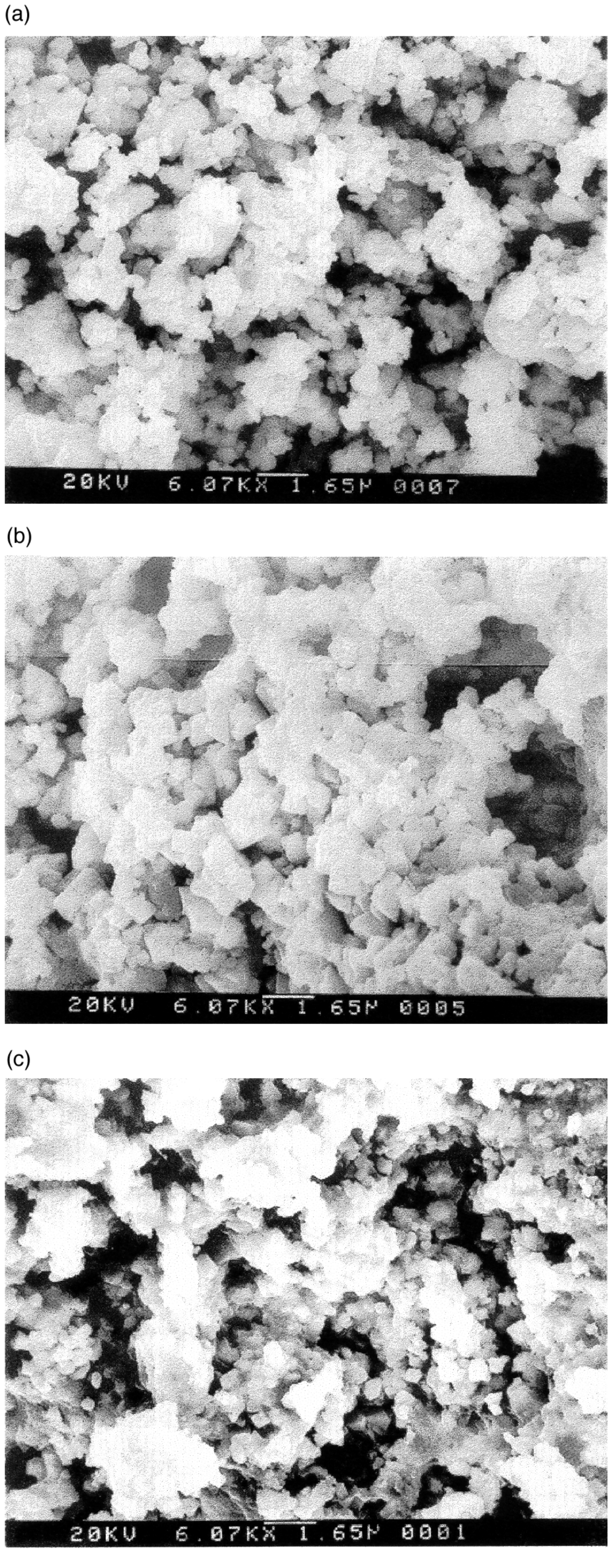

Fig. 3 SEM micrographs of (a) initial $Li_{0.5}Fe_{2.5}O_4$ powder, (b) product of reaction (3) at 700 °C for 10 h after washing out soluble components and (c) a mixture of $Li_{0.5}Fe_{2.5}O_4$ and $ZnSO_4$, annealed at 700 °C for 1 min.

ferrite, $LiFeO_2$, which can react with zinc sulfate by reaction (4)

$$2LiFeO_2 + ZnSO_4 \rightarrow ZnFe_2O_4 + Li_2SO_4 \qquad (4)$$

In this case 1 mol of ferrite product is accompanied by five times as much Li_2SO_4 compared to reaction (3). Formation of thermodynamically stable compounds of alkali or alkaline earth metals is believed to be the main driving force for SSM reactions,[3] so that reaction (4) should occur more readily. The relation between thermodynamic and kinetic considerations is rather controversial, but in this case, annealing of a pelletized mixture of lithium orthoferrite and zinc sulfate resulted in a much faster SSM reaction [Fig. 2(b)] which was complete at 700 °C within 15 min.

Analysis of SEM micrographs demonstrates the important contribution of diffusion processes to SSM. This is illustrated, for example, by definite growth of ferrite particles during the metathesis reaction [Fig. 3(a), (b)]. Another even more important feature of the process, as evidenced by SEM, is appearance of traces of a liquid phase at the intermediate stage of the process [Fig. 3(c)]. A possible reason for the absence of Li_2SO_4 reflections might be poor crystallization of the sulfate melt. The presence of liquid phases seems also to be a more probable reason for the unusually high rate of solid state reaction at 700 °C, rather than the phase transition for $ZnSO_4$. The rate of reaction (3) is fairly high even at 650 °C, when no transformation occurs for pure $ZnSO_4$ [Fig. 2(b)]. There is no data concerning melting of $ZnSO_4$ during thermolysis, while the melting point of pure Li_2SO_4 is *ca.* 860 °C. The presence of the molten sulfate matrix might be due to formation of low-temperature eutectics at the applied reaction temperatures, but more careful investigation is required to confirm this.

The presence of water or water vapour is believed to be an important factor which may complicate or even prevent SSM processes and many solid state reactions are carried out in dry-boxes or dried gas-filled reactors due to use of moisture-sensitive precursors.[3] Substituting $ZnSO_4$ for $ZnSO_4{\cdot}7H_2O$ in reaction (4) however had no effect, the rate of $ZnFe_2O_4$ formation remaining almost unchanged; no direct indication of a different reaction mechanism or appearance of new byproducts is observed. The reason for such behavior is complete dehydration of $ZnSO_4$ below the reaction temperature [eqn. (5)].[10]

$$ZnSO_4{\cdot}7H_2O \rightarrow ZnSO_4{\cdot}6H_2O \rightarrow ZnSO_4{\cdot}4H_2O \rightarrow ZnSO_4{\cdot}H_2O \rightarrow ZnSO_4 \quad (5)$$

Further practical application of these processes needs more careful studies of the reaction mechanism. Lithium ferrospinel is known to form an extensive range of solid solutions with zinc ferrite while the Li/Zn ratio has a dramatic influence on the magnetic properties of the ferrite materials.[11,12] Formation of such phases during SSM appears likely and possible practical applications depend on further investigations in this field.

The reaction described here is likely to be just one of an extensive set of similar processes. Anhydrous sulfates can be obtained for ferrite-forming elements in many procedures. Formation of MSO_4 during thermal dehydration of $MSO_4{\cdot}xH_2O$ is not specific for zinc sulfate and elimination of water from hydrated Cu, Ni, Mg and Co sulfates follows a similar pathway.[13] The chemical reactivity of sodium ferrite, and the stability and high solubility of Na_2SO_4 suggest SSM reactions of $NaFeO_2$ with sulfates to be feasible. We hope that this Communication will stimulate extensive studies of such interesting and potentially useful chemical processes.

Acknowledgments

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References

1 R. Rawlings, *Mater. World*, 1995, **3**, 474.
2 A. Neubrand and J. Rodel, *Z. Metallkd.*, 1997, **88**, 358.
3 E. G. Gillan and R. B. Kaner, *Chem. Mater.*, 1996, **8**, 333.
4 L. Rao, E. G. Gillan and R. B. Kaner, *J. Mater. Res.*, 1995, **10**, 353.
5 A. L. Hector and I. P. Parkin, *J. Mater. Chem.*, 1994, **4**, 279.
6 E. G. Gillan and R. B. Kaner, *Inorg. Chem.*, 1994, **33**, 5693.
7 S. Hilpert and A. Wille, *Z. Phys. Chem. B*, 1932, **18**, 291.
8 M. Spiess and R. Gruehn, *Z. Anorg. Allg. Chem.*, 1979, **456**, 222.
9 W. Reche and R. Landsberg, *Z. Anorg. Allg. Chem.*, 1970, **375**, 128.
10 K. Koehler and P. Zaeske, *Z. Anorg. Allg. Chem.*, 1964, **331**, 1.
11 R. E. Camley and C. E. Patton, *J. Magn. Magn. Mater.*, 1986, **54–57**, 1601.
12 M. Seqqat, G. Nicoara, M. Nogues, J. L. Dorman and D. Sayah, *J. Magn. Magn. Mater.*, 1996, **157–158**, 489.
13 M. E. Brown, D. Dollimore and A. K. Galwey, *Reactions in the Solid State: Comprehensive Chemical Kinetics*, ed. C. H. Bamford and C. F. H. Tipper, Elsevier Science Publishing Co., Amsterdam–Oxford–New York, 1980, vol. 22.

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