PHYSICAL REVIEW B VOLUME 49, NUMBER 9 1 MARCH 1994-I

# Lithium glass in $Li_3Sc_{2-x}Fe_x(PO_4)_3$ crystals

S. Sigaryov* and V. G. Terziev
*Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia*

J-L. Dormann
*Laboratoire de Magnetisme, Centre National de la Recherche Scientifique, Bellevue, France*

(Received 24 May 1993; revised manuscript received 8 October 1993)

It is found that substitutions of Sc by Fe in $Li_3Sc_2(PO_4)_3$ and of Fe by Sc in the isostructural compound $Li_3Fe_2(PO_4)_3$ result in suppression of an order-disorder phase transition in the lithium subsystem of the $Li_3Sc_{2-x}Fe_x(PO_4)_3$ mixed crystals. Thus a lithium disorder, dominating at $T \geq 570$ K, is preserved at lower temperatures. This leads to a glassylike behavior of the crystals, in particular, Vogel-Fulcher-Tammann temperature dependence of the ionic conductivity.

A structural dynamic disorder of ions of one (or more than one) sort is the distinguishing feature of superionic conductors.[1] Mobility of the ions is comparable with that in liquids and melted electrolytes. This allows use of an "ionic liquid" approach to describe the behavior of the mobile-ion subsystem.[2]

With decreasing temperature most superionics undergo an order-disorder phase transition resulting in ordering of the mobile ions in the low-temperature phase.[3] This is a transition from dynamic disorder to static order or, within the above-mentioned approach, "crystallization" of the ionic liquid. However, in some cases an order-disorder phase transition in superionics is not observed with a temperature decrease down to almost 0 K. As a result, the high-temperature dynamic disorder gradually transforms to a low-temperature static disorder, in analogy to glass formation upon cooling of certain liquids. Thus, the subsystem of conducting ions reveals glasslike properties at low temperatures, as has been found experimentally.[4-6] The reasons leading to either crystallization or glassification of the mobile-ion subsystem are not yet clear.

This paper presents data on lithium ordering in $Li_3Sc_{2-x}Fe_x(PO_4)_3$ solid solutions. The end members of the corresponding quasibinary system, $Li_3Sc_2(PO_4)_3$ and $Li_3Fe_2(PO_4)_3$, are superionic conductors with $\sigma_{573\,K} \simeq 10^{-1}$ S cm$^{-1}$.[7,8] This means that the lithium subsystems of these compounds are disordered at high temperature. With decreasing temperature, structural phase transitions take place in both $Li_3Sc_2(PO_4)_3$ and $Li_3Fe_2(PO_4)_3$ within the range 700–500 K, which tend to order the lithium sublattices. This ordering process is much more pronounced for $Li_3Sc_2(PO_4)_3$ than for $Li_3Fe_2(PO_4)_3$. Taking into account that the order-disorder processes in these crystals seem to be governed by lithium-lithium interactions,[9] we suggest a different interaction strength in $Li_3Sc_2(Po_4)_3$ and $Li_3Fe_2(PO_4)_3$.

As was shown elsewhere,[10] atomic substitutions in the rigid skeleton, creating competing interactions in a coupled labile subsystem (e.g., ferro- and antiferroelectric), are able to preserve the high-temperature disorder in crystals down to very low temperatures. The goal of the present studies is to investigate the effect of atomic substitutions in the rigid skeleton on the behavior of the coupled labile subsystem for the case of an interaction of random strength.

All materials under investigation were synthesized using conventional procedures, whose description can be found elsewhere.[11] Characterization of these substances was carried out by x-ray diffraction (Rigaku Geigerflex D3 diffractometer, $\lambda = 1.5405$ Å), and confirmed that the products of the chemical reaction form a continuous range of solid solutions.

Mössbauer spectra of the substances were recorded in the temperature range 4.5–295 K with a conventional constant-acceleration spectrometer in transmission geometry. The $^{57}$Co(Cr) source with an activity of 50 mCi was at room temperature. The average background level of the Mössbauer spectra was $\simeq 5\times10^6$ per channel.

Electronic currents in the samples were measured by the Hebb-Wagner polarization technique.[12] The value of $\sigma_{el} < 10^{-8}$ S cm$^{-1}$ at 293 K is at least an order of magnitude lower than the total conductivity at this temperature. This confirms the ionic character of charge transfer in these solid solutions. Ionic conductivity measurements were performed using a complex-impedance technique in the frequency range $5-5\times10^5$ Hz and in the temperature interval 293–600 K (Tesla BM 507 impedance meter).

Differential-scanning-calorimetry studies of the mixed crystals were carried out in the temperature range 130–595 K (Perkin-Elmer DSC 7 unit). The precision of temperature control during all experiments was at least ±1 K.

Figure 1 shows $\sigma(T)$ and DSC curves of $Li_3Sc_{2-x}Fe_x(PO_4)_3$ with increasing $x$. As can be seen from Fig. 1, an order-disorder phase transition resulting in both a stepwise increase of $\sigma$ and a $\lambda$-type anomaly in the DSC trace is simultaneously suppressed and shifted to the low-temperature range as $x$ increases from 0.0 to 0.4. Similar but much more pronounced behavior is ob-

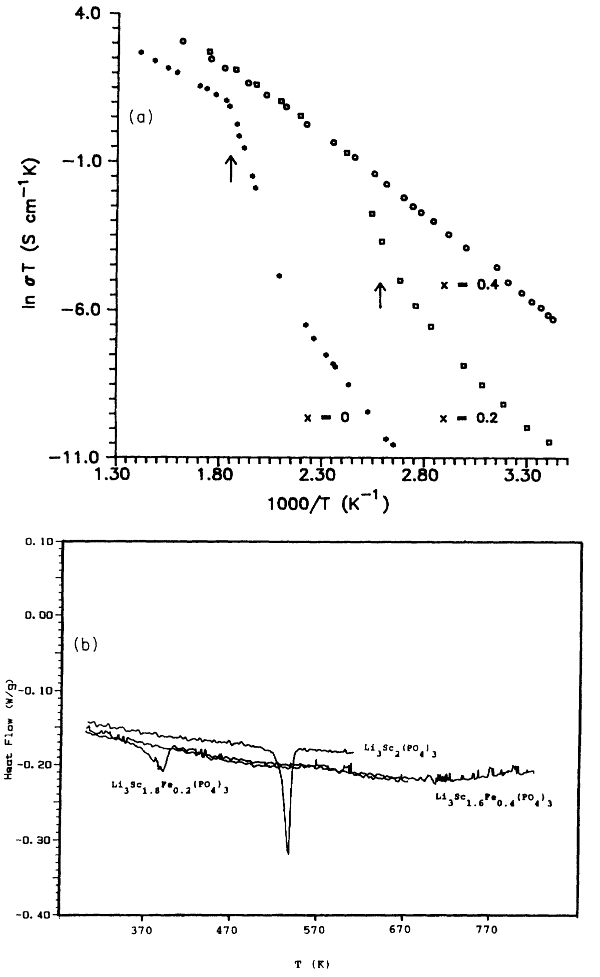

FIG. 1. (a) Arrhenius plot of the temperature dependence of the ionic conductivity of $Li_3Sc_{2-x}Fe_x(PO_4)_3$ mixed crystals for $0.0 \leq x \leq 0.4$ (arrows indicate the temperatures of order-disorder transformations). (b) DSC traces of the $Li_3Sc_{2-x}Fe_x(PO_4)_3$ mixed crystals for $0.0 \leq x \leq 0.4$.

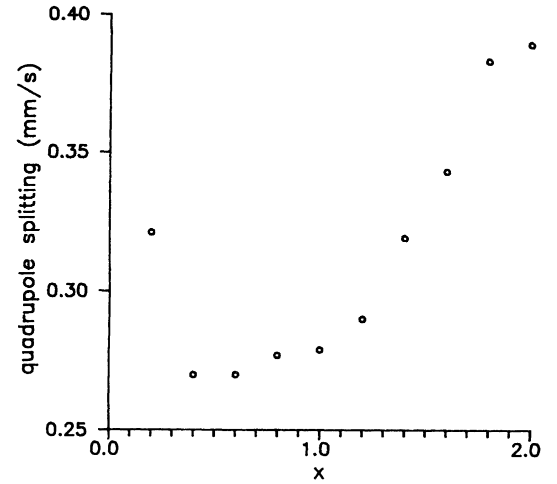

FIG. 2. Concentration dependence of the quadrupole splitting from $^{57}$Fe Mössbauer spectra of $Li_3Sc_{2-x}Fe_x(PO_4)_3$ mixed crystals at 295 K.

served for decrease of $x$ from 2.0 [anomalies in both the $\sigma(T)$ and $C_p(T)$ curves have disappeared already at $x = 1.8$].

Taking into account that this order-disorder transformation is caused only by processes in the lithium sublattices, we suggest that the lithium subsystem remains disordered down to 293 K for $0.2 \leq x < 2.0$. This suggestion is confirmed by the relatively high ionic conductivity of the $Li_3Sc_{2-x}Fe_x(PO_4)_3$ mixed crystals at 293 K ($\simeq 10^{-6}$ s cm$^{-1}$).

DSC studies of the solid solutions for $0.2 < x < 2.0$ indicate the absence of $C_p(T)$ anomalies in the temperature range down to 130 K. Comparison of the Raman spectra of the solid solutions at 77 K (Ref. 13) with the spectra of pure $Li_3Sc_2(PO_4)_3$ and $Li_3Fe_2(PO_4)_3$ (Ref. 14) indicates that significant disorder in the lithium subsystem still exists at 77 K, at least in the range $0.8 \leq x \leq 1.2$.

Figure 2 shows the concentration dependence of the quadrupole splitting $\Delta E_q$ on the $^{57}$Fe nuclei in $Li_3Sc_{2-x}Fe_x(PO_4)_3$ at 295 K. As was shown elsewhere,[15] the temperature behavior of $\Delta E_q$ is governed by order-disorder processes in the sublattice of the mobile ions: the higher the disorder, the lower the value of the quadrupole splitting. As can be seen from Fig. 2, at room temperature the substitution of Sc by Fe results in lithium disorder for all the solid solutions. The disorder reaches a maximum for $0.4 < x \leq 1.2$.

With decreasing temperature, some ordering of the lithium subsystem takes place between 295 and $\simeq 50$ K (see the increase of $\Delta E_q$ in Table I). However, the values of $\Delta E_q$ at the lowest temperatures studied do not reach the corresponding magnitude of $\Delta E_q$ for $Li_3Fe_2(PO_4)_3$ at 295 K. This means that the lithium subsystem of the mixed crystals remains more disordered than the lithium subsystem of $Li_3Fe_2(PO_4)_3$ at 295 K (note that $Li_3Fe_2(PO_4)_3$ is a more disordered compound than $Li_3Sc_2(PO_4)_3$ at 295 K according to the ionic-conductivity data[15,16]). Thus, there is lithium disorder in these solid solutions even at very low $T$ (for example at 4.5 K for $x = 0.4$).

It is clear that this lithium disorder preserved from high temperatures cannot maintain its dynamic character in the low-temperature range. In other words, a gradual transition from dynamic to static disorder should occur

TABLE I. Values of the quadrupole splitting ($\Delta E_q$) of $^{57}$Fe for $Li_3Sc_{2-x}Fe_x(PO_4)_3$ mixed crystals at various values of $x$ and $T$.

| Concentration $x$ | Temperature (K) | $\Delta E_q$ (mm/s) |
|---|---|---|
| 1.6 | 293 | 0.343 |
|  | 51 | 0.384 |
|  | 35 | 0.361 |
| 1.4 | 293 | 0.319 |
|  | 24 | 0.369 |
| 0.4 | 293 | 0.263 |
|  | 35 | 0.308 |
|  | 15 | 0.305 |
|  | 4.5 | 0.313 |

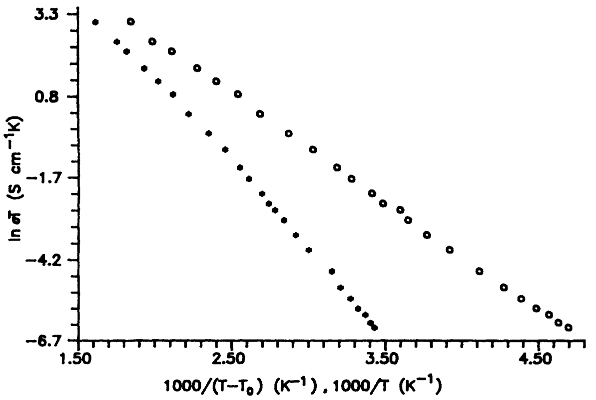

FIG. 3. Arrhenius (∗) and Vogel-Fulcher-Tammann (o) plots of the temperature dependence of the ionic conductivity of $Li_3Sc_{1.6}Fe_{0.4}(PO_4)_3$.

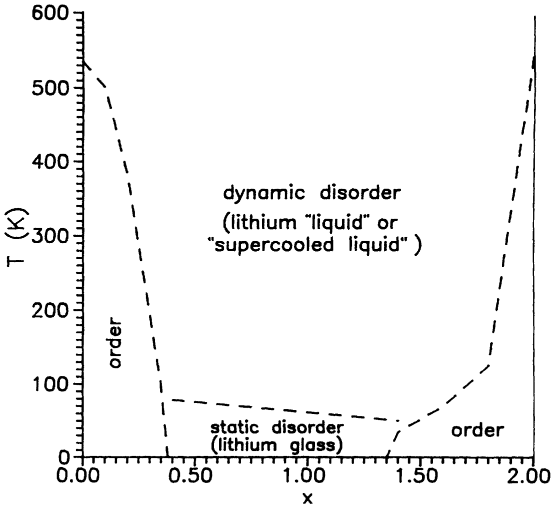

FIG. 4. Tentative phase diagram for the lithium subsystem in $Li_3Sc_{2-x}Fe_x(PO_4)_3$ mixed crystals.

with decreasing temperature. Static disorder means the appearance of a glasslike state in the lithium subsystem of the crystals, as was found earlier for other superionics: sodium β-alumina[4,5] and $Li_3N$.[6] Formation of a glassy state is usually accompanied by a glass transition.[17] From this point of view, taking into account the DSC data obtained, the temperature corresponding to the glass transition ($T_g$) in the $Li_3Sc_{2-x}Fe_x(PO_4)_3$ solid solutions seems to lie below 130 K. On the other hand, a glass transition results in changes of dynamic rather than structural parameters of a system, so one can find $T_g$ from the temperature behavior of dynamical characteristics of the crystals, such as ionic conductivity, which follows well-known Vogel-Fulcher-Tammann (NFT) law above $T_g$.[18]

Figure 3 shows, as an example, the $\sigma(T)$ curve for the $Li_3Sc_{1.6}Fe_{0.4}(PO_4)_3$ solid solution in both the Arrhenius and VFT frameworks. As can be seen from Fig. 3, this dependence shows distinct deviations from the Arrhenius law and can be described well within the VFT approach ($\sigma \propto \exp[-E_a^{\mathrm{VFT}}/k(T-T_0)]$, $T_0$ being a characteristic VFT temperature). Within the classical VFT approach, developed for the description of the temperature behavior of viscosity of liquids, the temperature $T_0$ corresponds to $T_g$. The $T_0$ value obtained by fitting the temperature behavior of the ionic-conductivity data of the $x=0.4$ sample is about of 78±2 K. This value agrees with the DSC and Raman light-scattering data.

Thus, we suggest that the dynamic lithium disorder in $Li_3Sc_{1.6}Fe_{0.4}(PO_4)_3$ is "frozen in" below $\simeq 78$ K. As follows from the Mössbauer-spectroscopy data (see Table I), this disorder is maintained down to 4.5 K. Thus a lithium glass state appears in this crystal. A similar process seems to occur in $Li_3Sc_{2-x}Fe_x(PO_4)_3$ at other values of $x$ between 1.6 and 0.4. Figure 4 shows a tentative phase diagram of the system.

As was mentioned above, atomic substitutions in the rigid skeleton of the $Li_3M_2(PO_4)_3$-type compounds do not lead to the appearance of competing interactions within the labile subsystem, unlike the case of RADP proton glasses.[9,10] On the other hand, interaction between the lithium ions are different for $Li_3Sc_2(PO_4)_3$ and $Li_3Fe_2(PO_4)_3$: in the first compound, they result in the distinct order-disorder phase transition at $\simeq 535$ K, while in the second crystal, lithium disorder is thermally induced[15] and the phase transitions result only from a change of activation energy for formation of the defects.

These significant differences in behavior of the mobile ions seem to depend on the chemical composition of the crystals, i.e., the type of $M$ cation in the rigid skeleton (because there is no difference in the atomic structure of the compounds). Qualitatively we can suggest that lithium-lithium interactions are significantly suppressed in $Li_3Fe_2(PO_4)_3$ compared to $Li_3Sc_2(PO_4)_3$. The origin of the suppression needs further investigation. For example, it may be due to more significant screening of the Coulomb forces in the lithium iron phosphate than in the lithium scandium phosphate, caused by differences in the electron density distributions. In this case, substitution of Sc by Fe or vice versa will lead to spatial randomization of the interaction strength in the lithium subsystem. This is qualitatively equal to the introduction of a second alternative force in the lithium-lithium interactions. In other words, the situation can be reduced to the above-mentioned case of proton glasses.

In conclusion, a glass-type state in $Li_3Sc_{2-x}Fe_x(PO_4)_3$ solid-solution crystals appear as a result of "freezing" of the high-temperature dynamical lithium disorder. The "freezing" is stimulated by Sc↔Fe substitutions in the rigid skeleton.

The authors wish to thank Dr. O. Melnikov and S. Doronin for synthesis of the $Li_3Sc_{2-x}Fe_x(PO_4)_3$ mixed crystals and Dr. V. Sinitsyn for performing the DSC studies at low temperatures.

[*] Author to whom all correspondence should be addressed. Present address: Institut für Physikalische Chemie, Schlossplatz 4, Münster 48149, Germany.

[1] S. M. Shapiro and F. Reidinger, in *Physics of Superionic Conductors,* edited by M. S. Salamon (Springer, Berlin, 1979), p. 45.

[2] H. Sato, in *Solid Electrolytes,* edited by S. Geller (Springer, Berlin, 1977), p. 3.

[3] M. B. Salamon, in *Physics of Superionic Conductors* (Ref. 1), p. 175.

[4] D. B. McWhan, C. M. Varma, F. L. S. Hsu, and J. P. Remeika, Phys. Rev. B **15**, 553 (1977); P. J. Anthony and A. C. Anderson, *ibid.* **16**, 3827 (1977).

[5] K. L. Ngai and U. Strom, Phys. Rev. B **27**, 6031 (1983).

[6] T. Baumann, M. V. Schickfus, S. Hunklinger, and J. Jäcle, Solid State Commun. **35**, 587 (1980).

[7] E. A. Genkina, L. N. Demyanets, A. K. Ivanov-Shits, B. A. Maximov, O. K. Melnikov, and V. I. Simonov, Pisma Zh. Eksp. Teor. Fiz. **38**, 257 (1983).

[8] F. d'Yvoire, M. Pintard-Screpel, E. Bretey, and M. de la Rochere, Solid State Ionics **9&10**, 851 (1983).

[9] S. E. Sigaryov, Mater. Sci. Eng. B **13**, 121 (1992).

[10] E. Courtens, J. Phys. (Paris) Lett. **43**, L199 (1982); V. H. Schmidt, S. Waplak, S. Hutton, and P. Schnackenberg, Phys. Rev. B **30**, 2795 (1984).

[11] A. B. Bykov *et al.*, Solid State Ionics **38**, 31 (1990).

[12] C. Wagner, Z. Elektrochem. **60**, 4 (1956).

[13] V. I. Michailov, S. E. Sigaryov, and V. G. Terziev, SPIE **1590**, 203 (1991).

[14] V. V. Kravchenko, V. I. Michailov, and S. E. Sigaryov, Solid State Ionics **50**, 12 (1991).

[15] S. E. Sigaryov and V. G. Terziev, Phys. Rev. B **48**, 16252 (1993).

[16] S. E. Sigaryov, Solid State Commun. **75**, 1005 (1990).

[17] A. R. West, *Solid State Chemistry and its Applications* (Wiley, Chichester, 1987), p. 594.

[18] *Proceedings of the International Discussion Meeting on Relaxation in Complex Systems,* edited by K. L. Ngai and G. B. Wright [J. Non-Cryst. Solids **131-133** (1991)].