The Synthesis and Characterization of LiFeAs Superconductor by XPS Method

Maria Kanuchova*[a], Lubica Kozakova

[a]The Technical University of Kosice, Faculty of Mining, Ecology, Process Control and Geotechnology, Institute of Montaneous Sciences and Environmental Protection, Park Komenskeho 19, 043 84 Kosice, Slovakia

maria.kanuchova@tuke.sk

Oxypnictide materials are known for a complexity of their methods of preparation. In a previous paper an advantage of the small atomic radius of Li was taken in employment an electrochemical method to insert Li into the precursor FeAs to form LiFeAs at room temperature. The electrolyte was a liquid mixture of ethyl carbonate, diethyl carbonate, lithium hexafluorophosphate, and ethyl methyl carbonate in equal amounts by volume.

In this work we present a simple electrochemical method of LiFeAs preparation by electrolysis in open air from molten LiCl electrolyte (melting point = 605 °C) with an inert electrode (graphite) as the anode and with FeAs pellet as the cathode. The superconducting transition temperature of the prepared LiFeAs material was about 17 K, which is consistent with the reported data. Obtained LiFeAs samples have been investigated by x-ray photoemission spectroscopy (XPS).

1. Introduction

Since the discovery of superconductivity in $LaFeAsO_{1-x}F_x$ (abbreviated as 1111) with T_c of 26 K, the FeAs based systems have attracted a great deal of research interest. Substituting La with other rare earth (RE) elements with smaller ion radii dramatically enhances the T_c up to 41 – 55 K (Chen et al., 2009). At room temperature, all these parent compounds crystallize in a tetragonal ZrCuSiAs-type structure, which consists of alternate stacking of edge-sharing Fe_2As_2 tetrahedral layers and RE_2O_2 tetrahedral layers along the c axis. Soon after this discovery, another group of compounds AFe_2As_2 (A = Ba, Sr, Ca) (122), which crystallize in a tetragonal $ThCr_2Si_2$ - type structure with identical Fe_2As_2 tetrahedral layers as in LaFeAsO, were also found to be superconducting with T_c up to 38 K upon hole doping (Chen et al., 2010). Except for the above systematically studied series of iron based superconductors, attempts have also been made to find iron-based superconductors with new structures, resulting in the discovery of superconductors such as AFeAs (Chen et al., 2009).

The characteristic building block for most iron pnictides is the layer of Fe and As ions which is believed to be the active layer for superconductivity (similar to the CuO_2 layers in high-T_c cuprates). The Fe-3d orbitals are hybridized with the As-4p states and each iron ion is tetrahedrally coordinated to four arsenic ions. The active layers are separated by charge reservoir blocks that can be chemically altered to control the charge doping in the FeAs layers. At the early stage of iron pnictides research, it was greatly important to reveal the basic electronic structure of these newly-discovered materials and to see whether and to what extent they are similar to the cuprates. For example, it is well known that strong electron correlation plays a major role in the high-T_c cuprates, while it is not clear to what extent this applies to iron pnictides. Also, strong p-d hybridization exists in the cuprates, whereas no clear idea on this is known for pnictides. While there are theoretical attempts at understanding the basic electronic structure of these compounds experimental indications which distinguish these new high-T_c superconductors from the other superconductors are desirable. Some theoretical works imply the importance of electron correlations, and their effects on the unconventional superconductivity (Gooch et al., 2010).

LiFeAs crystallizes in the tetragonal PbFCl type (P4/nmm) with a = 3.7914 Å and c = 6.364 Å. The Fe_2As_2 charge carrying layers are alternatively stacked along the c-axis with nominal double layers of Li ions. The superconducting behaviour of LiFeAs (the formal charge balance $Li^{1+}Fe^{2+}As^{3-}$) can be roughly explained by assuming incomplete charge transfer from the strongly polarizing Li atoms to the electron-rich $(Fe_2As_2)^{2-}$ layers. However, this would lead to a hole-like behavior of the carriers, which is in conflict with the thermoelectric power data (Tapp et al., 2008).

The inconsistency may arise from changes in the conduction bands of the FeAs layers due to variations in inter-layer distances. LiFeAs at ambient physical pressure may reside in the equivalent high-pressure state of other undoped iron pnictides due to the chemically induced lattice contraction. This would be consistent with the missing spin density wave state, the observed superconductivity at relatively high T_c, as well as with the negative linear pressure shift of T_c (Gooch et al., 2010). In order to check the charge balance in LiFeAs, we investigated the core-level and valence-band (VB) spectra by x-ray photoemission spectroscopy (XPS) which is a very powerful tool to directly probe the electronic structure of solids.

2. Sample preparation

LiFeAs was prepared by a new electrochemical method described in detail in (Kanuchova et al., 2013). A FeAs pellet (7 mm in diameter and 2 mm in thickness) served as the cathode electrode. High purity LiCl (99.9 %, ultra dry) was used as the electrolyte. A top-loading crucible furnace provided a temperature control of the electrolyte. The operation temperature was set to 610 ^{o}C, which is slightly above the melting point of LiCl at ambient pressure (605 ^{o}C). The electrochemical process was done at a voltage of 10 V provided by a dc power supply which worked in a regime of a constant voltage source. The current was < 0.2 A during the process.

3. Results and discussion

A stereo microscope top view of the pellet prepared by the present method as well as its cross-section is shown in Figure 1. The central part is unreacted FeAs, next to it is the LiFeAs layer followed by an excess of Li on the surface of the pellet. The chemical composition of LiFeAs prepared by electrochemical method was confirmed by X-ray photoelectron spectroscopy (XPS). XPS measurements were performed using XPS instrument (SPECS) equipped with PHOIBOS 100 SCD and non-monochromatic X-ray source. The survey surface spectrum was measured at 70 eV transition energy and core spectra at 20 eV at room temperature. All spectra were acquired at a basic pressure 2×10^{-8} mbar with MgK_α excitation at 15 kV (250 W). The data was analysed by SpecsLab2 CasaXPS software (Casa Software Ltd). A Shirley and Tougaard type baseline was used for all peak-fits.
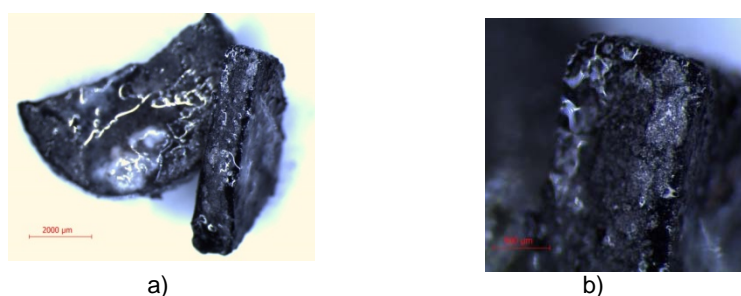

a)   b)

Figure 1: A stereo microscope cross-section of the FeAs pellet with a LiFeAs layer on its surface (a) and its magnified view (b)

a) XPS analysis of FeAs precursor

Figure 2 shows the XPS valence-band spectra of the FeAs sample. The spectrum of FeAs consists of six main bands centered around 710 eV, 530 eV, 285 eV, 143 eV, 53 eV and 43 eV. Carbon and oxygen are ubiquitous and are present on all surfaces for XPS analysis. It is common practice to use the carbon C 1s peak at 285 eV as a reference for charge correction. In routine XPS analyses of samples prepared outside the high vacuum chamber relatively thick carbon layers are formed on the surfaces, and the corrected XPS peak positions are independent of the apparent or experimentally obtained binding energy. The XPS

peaks of Fe 2p3/2 and Fe 2p1/2 for the FeAs sample are shown in Figure 3. Of the two Fe peaks the Fe 2p3/2 peak is stronger than Fe 2p1/2 and the area of Fe 2p3/2 peak is greater than that of Fe 2p1/2. The peak position of Fe 2p3/2 has been investigated by many researchers and the values between 710.6 and 711.2 eV have been reported (Yamashita T. and Hayes, P., 2008). The Fe 2p3/2 peak has an associated satellite peak. It has been shown in previous studies that the peak positions of Fe 2p1/2 and Fe 2p3/2 depends on the ionic states of Fe. The positions of the satellite peaks for the Fe 2p1/2 and Fe 2p3/2 peaks are also very sensitive to the oxidation states. The satellite peak of Fe 2p3/2 for Fe^{3+} is located approximately 5 eV higher than the main Fe 2p3/2 peak (Yamashita T. and Hayes, P., 2008). The binding energies of Fe 2p3/2 and Fe 2p1/2 obtained from the present study are 710.219 eV and 722.64 eV, respectively. The satellite peak obtained at 717.6 eV is clearly distinguishable – from this we can assume a presence of Fe^{3+} cation. The 143.6 eV As 3p spectrum of FeAs is dominated by the signal from As atoms (Figure 4). The As 3p peak has typical 3p 3/2 part – it can be assigned to As $^{3-}$ anion. The XPS spectrum for FeAs is clear and apart from C and O, without impurities, which is consistent with the XRD analysis.
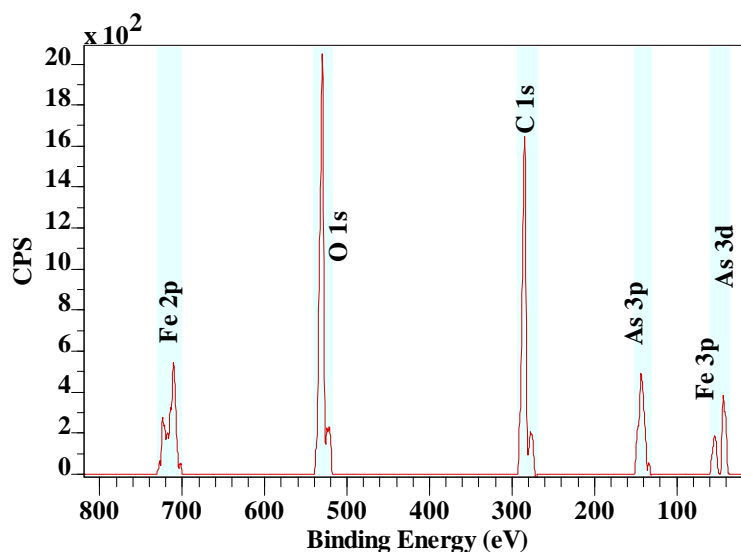

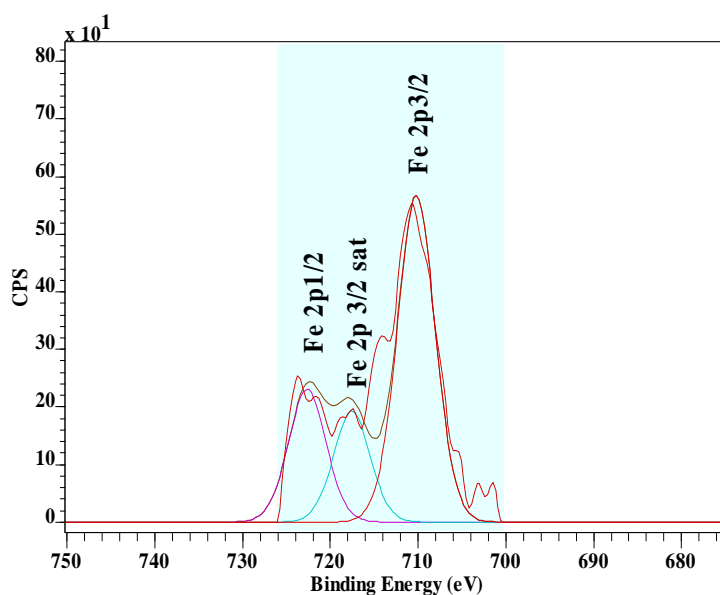*Figure 2: XPS valence-band spectra of the FeAs precursor sample.*

Figure 3: XPS valence-band spectra of Fe 2p ½ and 2p 3/2 – they indicate a presence of Fe^{3+} cation

b) XPS analysis of LiFeAs sample

Figure 5 shows the spectrum of LiFeAs. Compared with FeAs precursor there are visible changes. The spectrum of LiFeAs consists of eight main bands centered at around 711 eV, 532 eV, 285 eV, 199 eV, 144 eV,102 eV, 55 eV and 45 eV. The Li 1s core level XPS spectrum in Figure 6 is symmetric and centered at 55 eV which is attributed to the Li $^+$ cation. In Figure 7 we can see changes in the XPS peaks of Fe 2p3/2 and Fe 2p1/2 for the LiFeAs (as compared with FeAs precursor spectra in Figure 3). The electronic configuration of Fe^{2+} is 3d^6 whilst that of Fe^{3+} is 3d^5. It means that the peak of Fe^{2+} is smaller than Fe^{3+} peak, which is consistent with (Yamashita T. and Hayes, P., 2008). There exist interesting changes in XPS peak of As (Figure 8). Compared with FeAs precursor spectra (Figure 2) the spectrum of As in LiFeAs has two main peaks (Figure 5). The spectrum of As has two main peaks. The 198.3 eV As 3s spectra of LiFeAs are dominated by the signal from As atoms (Figure 5). The spectrum of As 3p is rapidly changed (Figure 8). It is broader and the 3p 3/2 peak indicates that As is As $^{5-}$ anion. This may be a result of a binding between the atoms in Li and As in LiFeAs.
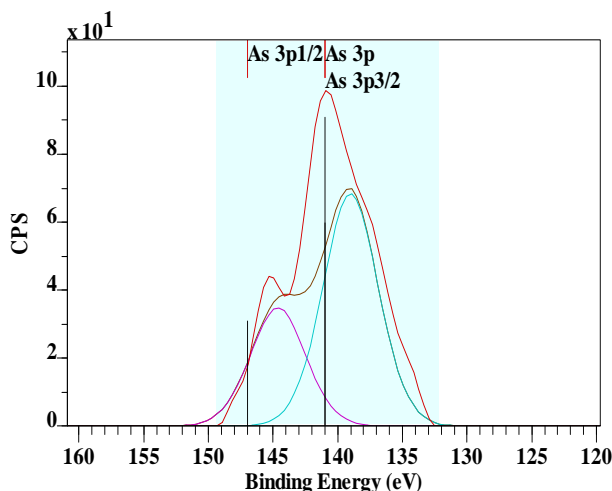

Figure 4: XPS valence-band spectra of As - they indicate a presence of As^{3-} anion
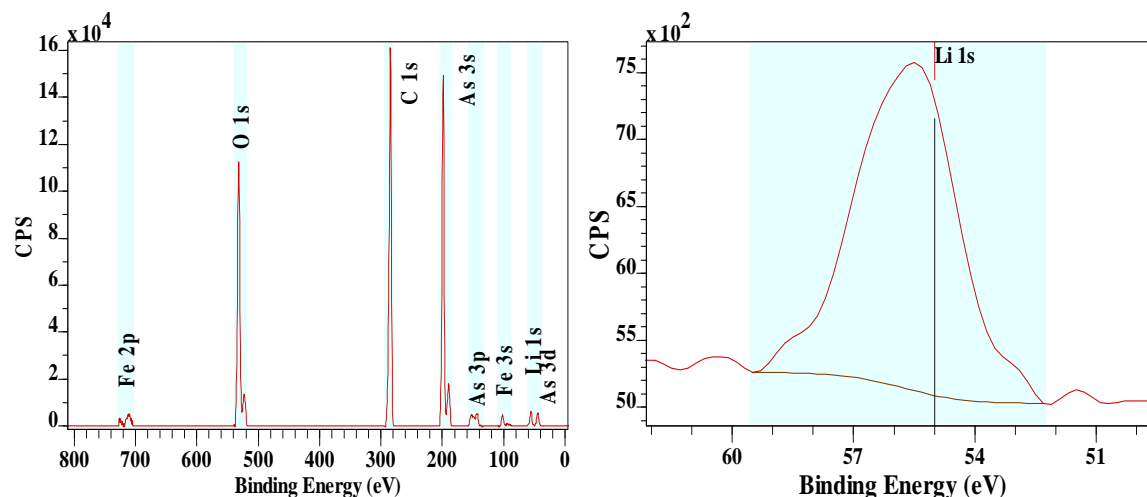

Figure 5: XPS valence-band spectra of LiFeAs

Figure 6: XPS valence-band spectrum of Li in LiFeAs - it indicates a presence of Li^{1+} cation
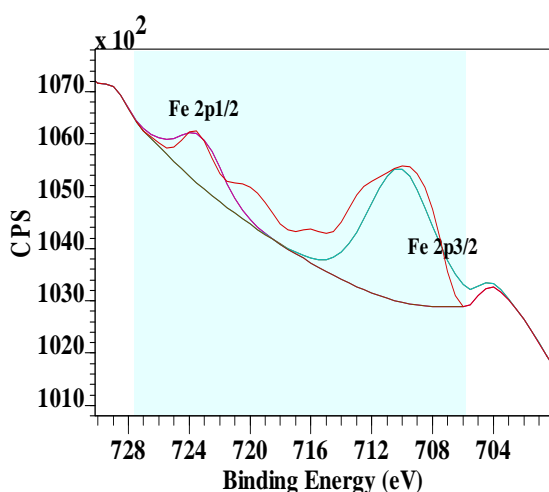
Figure 7: XPS valence-band spectra of Fe in LiFeAS – indicating a presence of Fe^{2+} cation
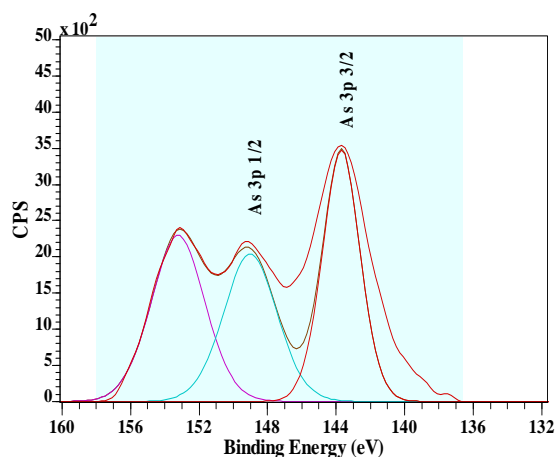
Figure 8: XPS valence-band spectra of As – they indicate a presence of As^{5-} anion

4. Conclusion

A successful preparation of LiFeAs sample using a simple electrochemical method has been presented. XPS results on FeAs precursor confirmed a presence of Fe^{3+} cations and As^{3-} anions, as expected. However, XPS results on LiFeAs indicate a presence of Li^{+}, Fe^{2+} cations and As atoms as well as As^{5-} anions. A big change in valency of As atoms may be caused by interaction with Li atoms. Atomic bonding for LiFeAs may be described in the following way in good agreement with the theoretical work of (Shein and Ivanovskii, 2010): (i) inside Fe_2As_2 blocks, mixed covalent - ionic bonds Fe-As take place (owing to hybridization of Fe 3d - As 3p states and Fe - As charge transfer); (ii) inside Fe_2As_2 blocks, metallic-like Fe - Fe bonds appear owing to delocalized near - Fermi Fe 3d states; (iii) between the adjacent Fe_2As_2 blocks and Li sheets, ionic bonds emerge owing to Li - Fe_2As_2 charge transfer. A combination of Fe^{3+} cations with As^{5-} anions (observed in this work) results in 2 fre electrons in FeAs layer, i.e. 1 free electron per atom – a concentration typical for metals (Kittel, 1996). This finding supports the idea of n-type conductivity in LiFeAs which is in agreement with thermoelectric power data (Tapp et al., 2008).

Acknowledgments

References

Chen G. F., Xia T-L, Yang H. X., Li J. Q., Zheng P., Luo J. L. and Wang N. L., 2009, Possible high temperature superconductivity in a Ti-doped A-Sc-Fe-As-O (A = Ca, Sr) system, Superconductor Science & Technology, 22, DOI: 10.1088/0953-2048/22/7/072001

Chen N., Qu S.P., Li Y., Liu Y., Zhang R. and Zha, H.L., 2010, Synthesis of LiFeAs superconductor by electrochemistry at room temperature, Journal of Applied Physics, vol. 107, Article Number 09E123

Gooch M., Lv B., Sasmal K., Tapp J. H., Tang Z. J., Guloy A. M., Lorenz B. and Chu C. W., 2010, Superconductivity in ternary iron pnictides: AFe2As2 (A = alkali metal) and LiFeAs, Physica C 470, S276–S279.

Yamashita T., Hayes P., 2008, Analysis of XPS spectra of Fe2+ and Fe3+ ions in oxide matrerials, J. Appl. Surf.Sci. 254, 2441-2449.

Kanuchova M., Majoros M., Kanuch J., Ding Y., Sumption M.D. and Collings E. W., 2013, LiFeAs pnictide superconductor – a simple electrochemical method of preparation, IEEE Transactions on Applied Superconductivity, vol. 23, DOI: 10.1109/TASC.2012.2232953

Kittel C., 1996, Introduction to Solid State Physics, 7th edition, John Wiley & Sons, Inc.

Shein I.R., Ivanovskii A.L., 2010, Electronic properties of novel 6 K superconductor LiFeP in comparison with LiFeAs from first principles calculations , Solid State Communications 150, 152-156

Tapp J.H., Tang Z.J., Lv B., Sasmal K., Lorentz B., Chu P.C.W. and Guloy A. M., 2008, LiFeAs: An intrinsic FeAs-based superconductor with Tc = 18 K, Physical Review B, vol. 78, Article Number 060505