HIGH-FIELD EPR OF METAL-DOPED SODIUM ALANATES

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Introduction

Metal-doped sodium aluminum hydrides (alanates) are promising candidates for new hydrogen storage materials with high gravimetric hydrogen storage capacities. It was shown that doping with Ti and Fe enhances the performance of these materials [1]. The mechanism by which the dopants enhance the hydrogen storage capacity of the alanates is not known. We report on EPR experiments at X-band and at very high magnetic fields on Ti- and Fe-doped $NaAlH_4$ at various stages of preparation (as prepared, after ball-milling, and after thermal cycling with H_2(g)).

Experimental

X-band EPR experiments were done with a Bruker Elexsys E580 instrument. The high-field experiments were done on a home-built instrument at the NHMFL.

Results and Discussion

Figs. 1 and 2 show the results of the EPR experiments on the different preparations at X-band (9.65 GHz) and at 188.3 GHz.

Fig. 1: EPR on doped $NaAlH_4$ in X-band @ 6K

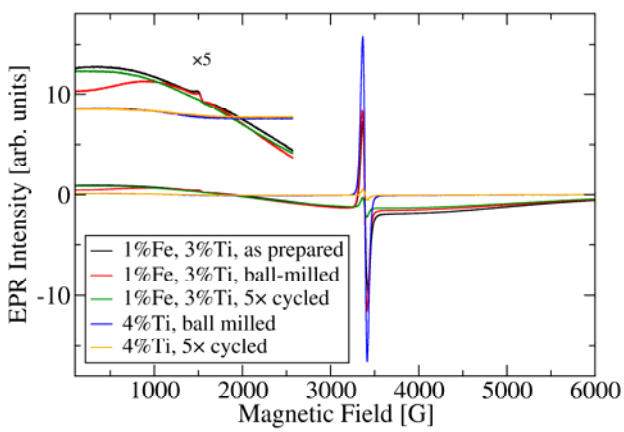
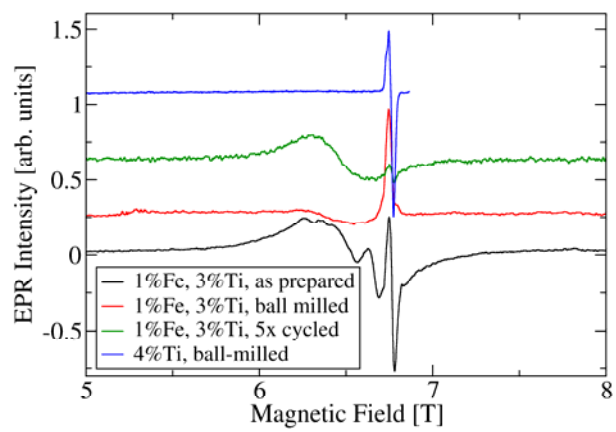


Fig. 2: High-Field EPR at 188.318 GHz @3-4 K



There are three EPR signals visible which can be tracked throughout the different preparations and may be used as markers of different paramagnetic forms of the dopants: 1. A relatively narrow signal of about 50 G linewidth at g = 1.989 (X-band) indicates the presence of Ti^{3+} in the samples. At high fields the g-factor remains the same but the line widens proportionally with the field strength (linewidth of 280 G at 188 GHz and 167 G at 95 GHz). This indicates a large amount of g-strain in this material. 2. A broad EPR line which isn't even fully resolved at X-band (3350 G linewidth at 188 GHz) appears at variable g = (2.082 @188 GHz, 2.095 @ 95 GHz, 2.9 @ 9.4 GHz) perhaps indicative of a high-spin species with fine structure. It definitely belongs to a Fe species of yet undetermined oxidation state 3. A very weak EPR signal at g = 4.4 is present in two of the Fe-containing samples and may be attributed to high-spin Fe^{3+} in the material. There are additional EPR signals visible in the high-field experiments that have not been identified, yet. Tracking the intensities of the Ti^{3+} and Fe signals shows that the amount of Ti^{3+} decreases after thermal cycling of the material in the presence of H_2(g). This might be due to conversion to metallic Ti(0) in the form of a Ti-Al alloy [2].

References

[1] Bogdanović, B., *et al.*, Journal of Alloys and Compounds, **302**, 36-58 (2000).
[2] Weidenthaler, C., *et al.*, Phys. Chem. Chem. Phys., **5**, 5149-5153 (2003).