

Dynamics of Thermal Decomposition of Solid Potassium Ferrate(VI) in Air by Means of in-situ NFS.

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Potassium ferrate(VI), K_2FeO_4 , with iron in oxidation state of (VI) decomposes under heat treatment around 500 K to $KFeO_2$ with iron in oxidation state (III). Detailed study of mechanism and kinetics of this transformation will contribute to a better understanding as well as optimization of the solid state synthesis of K_2FeO_4 . Moreover, the knowledge of the mechanism of the Fe(VI) reduction will be useful when explaining the mechanism of arsenic oxidation by the ferrate(VI). The mentioned technology based on the oxidation of arsenic by ferrate(VI) presents environmentally friendly route to remove arsenic from drinking and waste water [1-3].

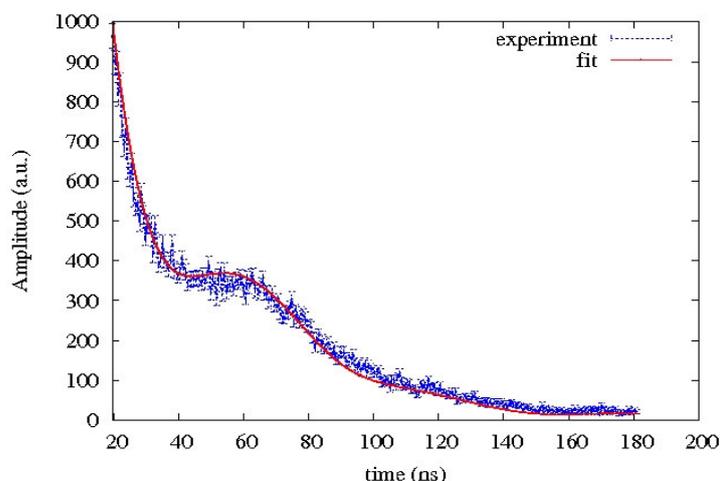


Figure 1: Nuclear Forward Scattering spectrum of K_2FeO_4 at room temperature. Solid line represents fit of experimental data by software CONUSS [5].

Recent investigations published in [4] confirmed the formation of potassium iron(III) oxide, $KFeO_2$, as primary iron containing decomposition product. Although in-situ approach was applied (in-situ variable temperature X-ray powder diffraction, in-situ high temperature Mössbauer spectroscopy and Thermal analysis), it was not possible to unambiguously confirm a formation of phases with tetravalent and/or pentavalent iron atoms during the transformation. Nuclear Forward Scattering (NFS) using synchrotron radiation presents practically the only experimental method which enables to obtain spectra of a sufficient quality within a very short time window (several seconds) available.

NFS of synchrotron radiation were carried out during the more than one hour of annealing under isothermal conditions at 200 °C, 220 °C, 235 °C, and 250 °C. The NFS spectra were accumulated during approximately 60 s and registered. The initial ferrate(VI) was prepared by a

wet chemical synthesis [6] with using of ^{57}Fe labelled ferric nitrate as reactant. The product of the synthesis contained around 10 wt% of $\text{Fe}(\text{OH})_3$. Experimental data were evaluated with employing a CONUSS software [5]. The nuclear forward scattering spectrum of the initial ferrate(VI) sample together with a fit of experimental data suggesting two spectral components, i.e. a major singlet corresponding to K_2FeO_4 and a minor doublet, which belongs to ferric hydroxide impurity, is plotted in Figure 1.

A progress of NFS spectra during the thermal treatments at selected temperatures (235 °C and 250 °C) is displayed by using of “contour” graphs (Figure 2), where the spectral intensities are coded by colour spectrum. The x -axis represents the time delay after an excitation pulse of synchrotron radiation and the y -axis represents time from the beginning of the thermal treatment.

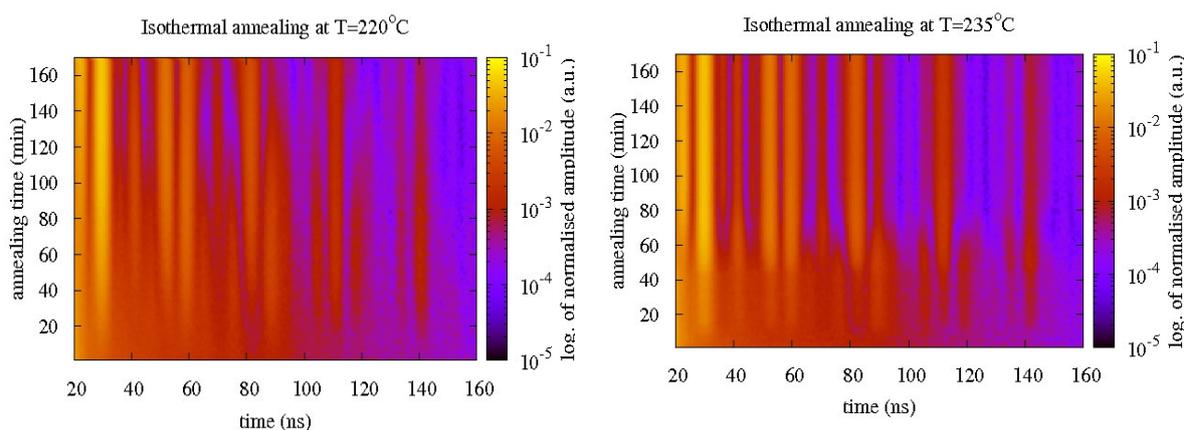


Figure 2: Nuclear Forward Scattering spectra obtained under isothermal reaction conditions at given temperature.

From changes of quantum beats [7] it is evident that temperature influences significantly the kinetics of the transformation (see Figure 2). Starting from precursors simple line shape of simple exponential decay modified by low amount of impurity determined by nonmagnetic state and ending at complicated structure of quantum beats caused by magnetic splitting of antiferromagnetically ordered KFeO_2 . The kinetics and mechanism of the transformation as well as eventual identification of Fe(IV) and/or Fe(V) phases is a subject of subsequent evaluations of the spectra and will be described in detail later.

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