

S. Michalik<sup>a</sup>, J. Bednarcik<sup>b</sup>, P. Pawlik<sup>c</sup>, R. Matija<sup>d</sup> and P. Sovak<sup>e</sup>

<sup>a</sup> Institute of Physics of the ASCR, v.v.i., Na Slovance 2, 182 21 Praha 8, The Czech Republic

<sup>b</sup> Deutsches Elektronen-Synchrotron, Notkestrasse 85, 22607 Hamburg, Germany

<sup>c</sup> Institute of Physics, Czestochowa University of Technology, Al. A. Krajowej 19, 42-200 Czestochowa, Poland

<sup>d</sup> Faculty of manufacturing technologies of Technical University of Kosice with a seat in Presov, Bayerova 1, 080 01 Presov, Slovakia

<sup>e</sup> Institute of Physics, Park Angelinum 9, 041 54 Kosice, Slovakia

## The aim

In this work the authors present the complete structural study of the as-prepared glassy  $\text{Fe}_{61}\text{Co}_{(14-x)}\text{Zr}_5\text{W}_x\text{B}_{20}$  ( $x = 1, 2$  and 4) ribbons and their structural evolution during thermal loading using the high energy X-ray diffraction (XRD).

## Experimental characterization

- ribbon samples of the composition  $\text{Fe}_{61}\text{Co}_{(14-x)}\text{Zr}_5\text{W}_x\text{B}_{20}$  ( $x = 1, 2$  and 4) were prepared by a melt spinning technique
- x-ray diffraction experiments were carried out in transmission mode at the beamline BW5 at HASYLAB/DESY at following conditions

- the wavelength  $\lambda = 0.1239 \text{ \AA}$
- beam size  $0.5 \times 0.5 \text{ mm}^2$
- illumination time 60 sec

- the sample treatment:

- ribbon materials were put into a capillary (diameter 2 mm) and heated by a two-lamp infrared furnace

25°C  $\xrightarrow{50^\circ\text{C}/\text{min}}$  200°C  $\xrightarrow{5^\circ\text{C}/\text{min}}$  800°C

## Characterization of the as-quenched samples

The structural factors  $S(Q)$  of the as-prepared  $\text{Fe}_{61}\text{Co}_{(14-x)}\text{Zr}_5\text{W}_x\text{B}_{20}$  ( $x = 1, 2$  and 4) alloys indicate the amorphous character of investigated samples. In all three cases,  $S(Q)$  seems to be almost identical. However a detailed inspection of the  $S(Q)_{x=2}$  revealed very low intensity Bragg peaks. On the other hand no crystalline traces were detected for ribbons with 1 and 4 at. % tungsten concentration.

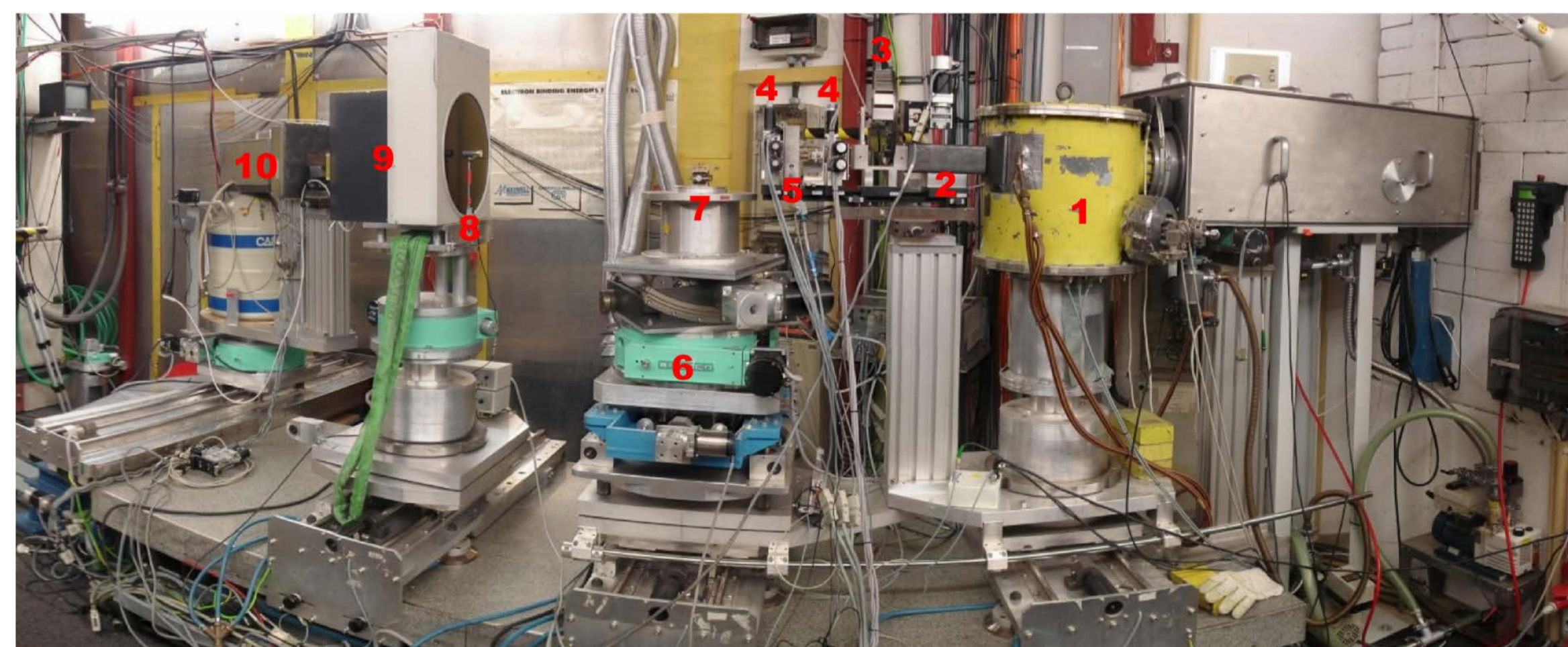
In order to obtain additional information about the (local) atomic arrangement in the as-prepared alloys, the total reduced atomic pair distribution functions  $D(r)$  were calculated [1]. The  $D(r)$ s are very similar and practically undistinguishable for higher  $r$  values (it is the true for the sample with  $x=2$  as well). Small changes are mainly seen on the first and second maxima which contain information about nearest coordination shells. The first maximum of the  $D(r)$  has strongly asymmetric shape suggesting the contribution of at least two subshells, maybe of three ones. The first shell could consist of atomic pairs of Fe-Fe and Fe-Co, the second one of Fe-W and the third one of Fe-Zr pairs. It is seen that the maximum position is slightly shifted from 2.565 Å to 2.580 Å with increasing W amount. This shift effect is a result of replacement of smaller Co atoms ( $r_{\text{Co}} = 1.253 \text{ \AA}$ ) by greater W ones ( $r_{\text{W}} = 1.37 \text{ \AA}$ ).

## In-situ XRD measurements

Using intensive synchrotron radiation offers an exclusive opportunity to follow structural changes during thermal loading. Firstly XRD profiles seem to be without any noticeable modification suggesting that samples persist in their original (amorphous) state. However marginal shifts of the main diffraction peak were detected and they were used for extraction of coefficients of thermal volume expansion  $\alpha_{\text{th}}$  of the amorphous phase following Yavari approach [2]. The values of  $\alpha_{\text{th}}$  are  $(3.00 \pm 0.06) \times 10^{-5} \text{ 1}^\circ\text{C}$ ,  $(3.40 \pm 0.10) \times 10^{-5} \text{ 1}^\circ\text{C}$  and  $(4.15 \pm 0.09) \times 10^{-5} \text{ 1}^\circ\text{C}$  for the samples with  $x = 1, 2$  and 4.

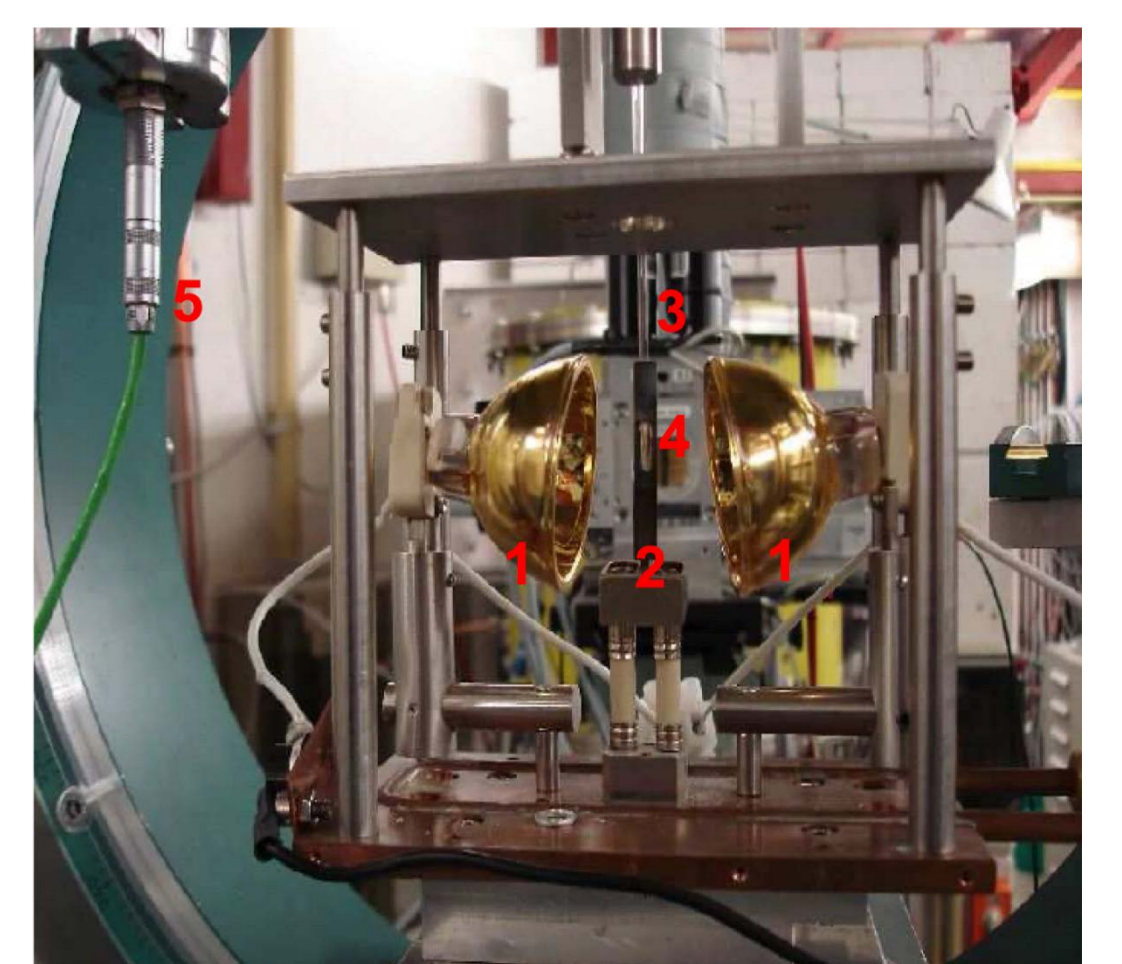
At certain point, Bragg peaks are appearing to indicate the beginning of the first crystallization. Formed Bragg peaks are indexed as the cubic  $\text{Fe}_{23}\text{B}_6$  phase. The low intensive Bragg peaks presented in the as-prepared  $\text{Fe}_{61}\text{Co}_{12}\text{Zr}_5\text{W}_2\text{B}_{20}$  ribbon could be index as the  $\text{Fe}_{73}\text{B}_6$  phase as well.

Photo of the experimental station BW5

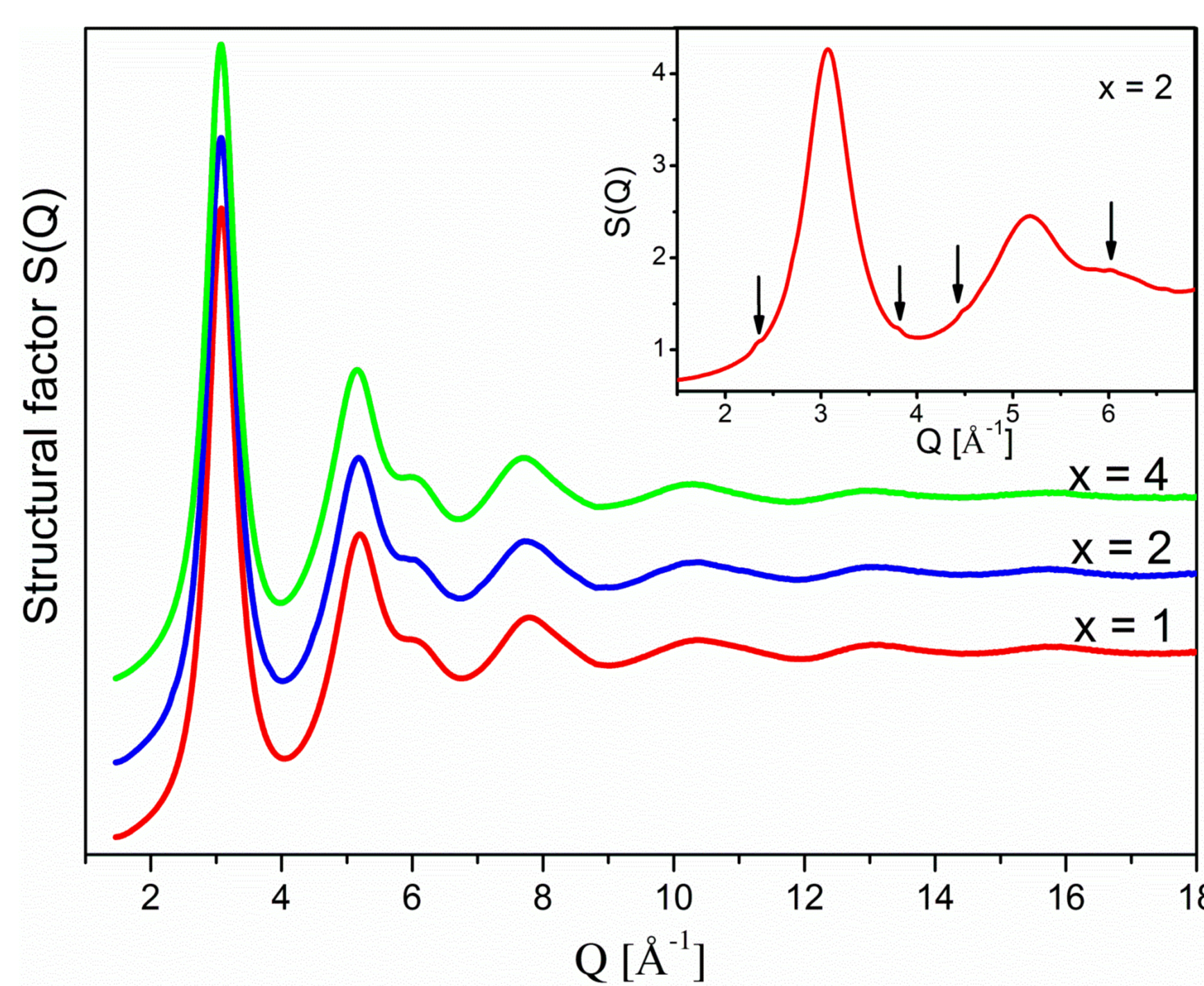


1 – tank with a monocrystal, 2 – colimator, 3 – steel revolving absorber, 4 – slits, 5- fast shutter, 6 and 7 – goniometer with a sample basement, 8 – beamstop, 9 – 2D MAR345 detector, 10 – solid stated detector

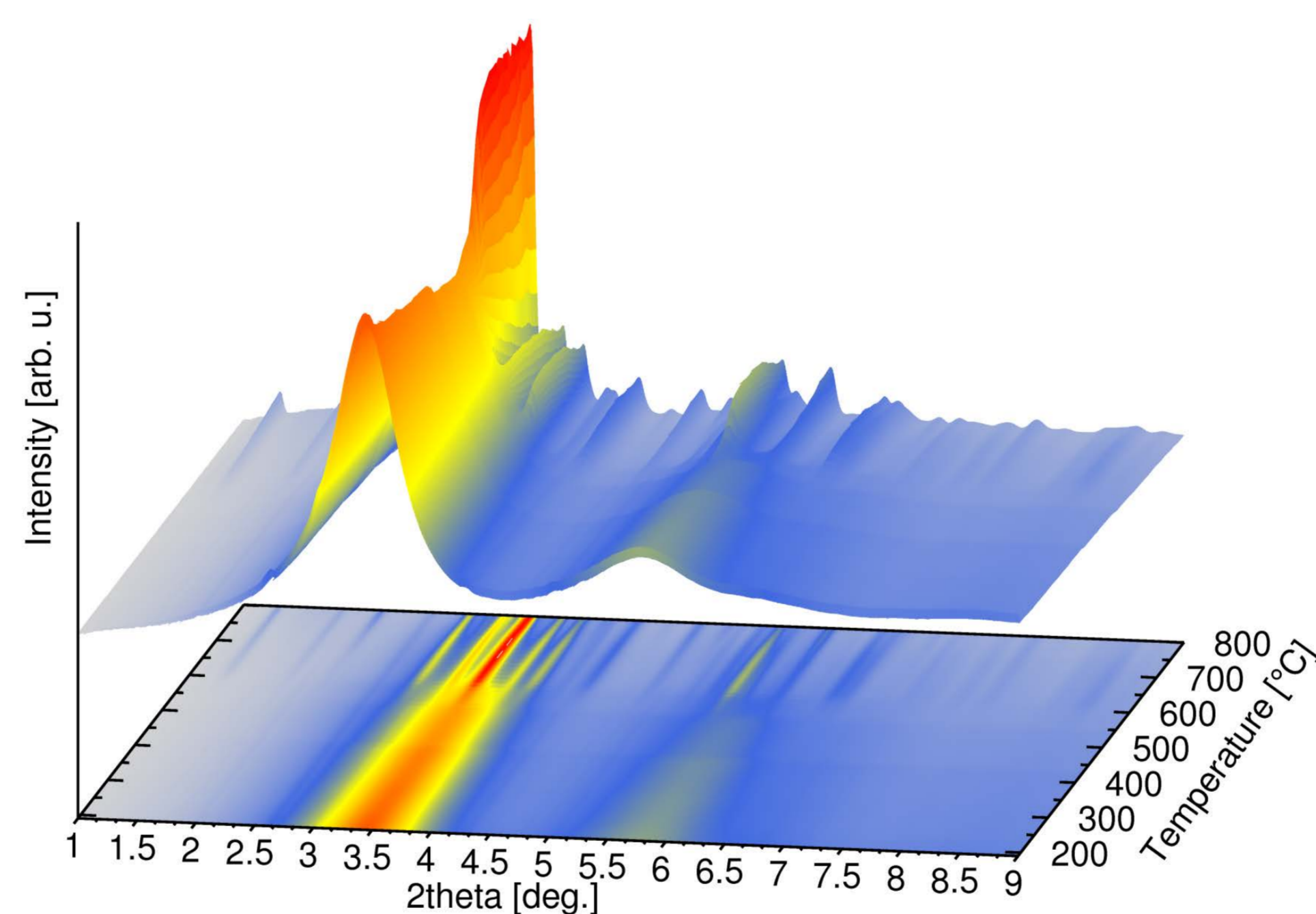
Photo of the infrared heater



1 – infrared lamps, 2 – capillary holder, 3 – capillary connected to a vacuum pump, 4 – capillary bottom with the sample material, 5 – thermocouple connector

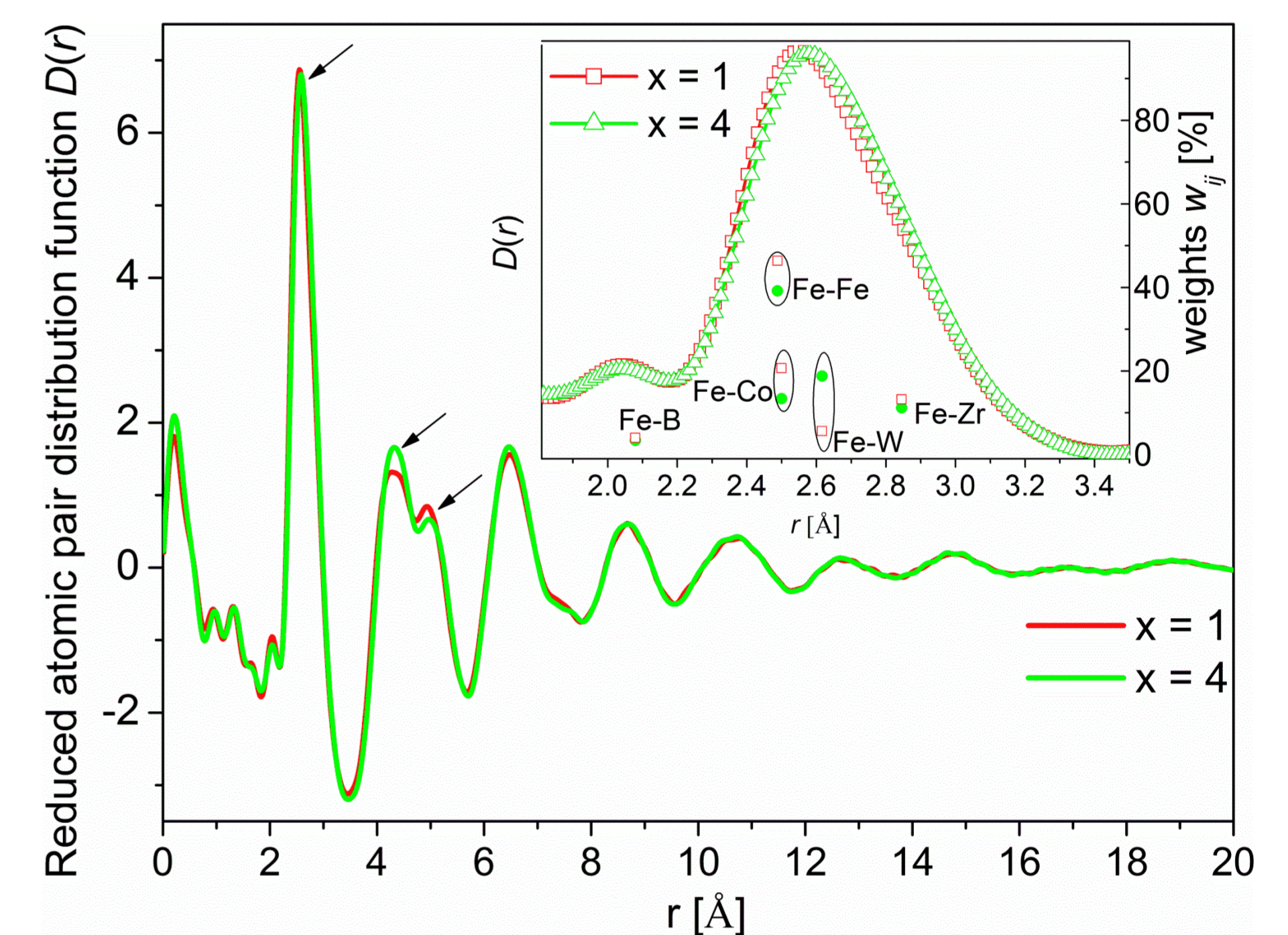


$S(Q)$ s of as-prepared  $\text{Fe}_{61}\text{Co}_{(14-x)}\text{Zr}_5\text{B}_{20}\text{W}_x$  samples. Insert at right upper corner shows in detail  $S(Q)_{x=2}$ . Arrows mark detected Bragg peaks.

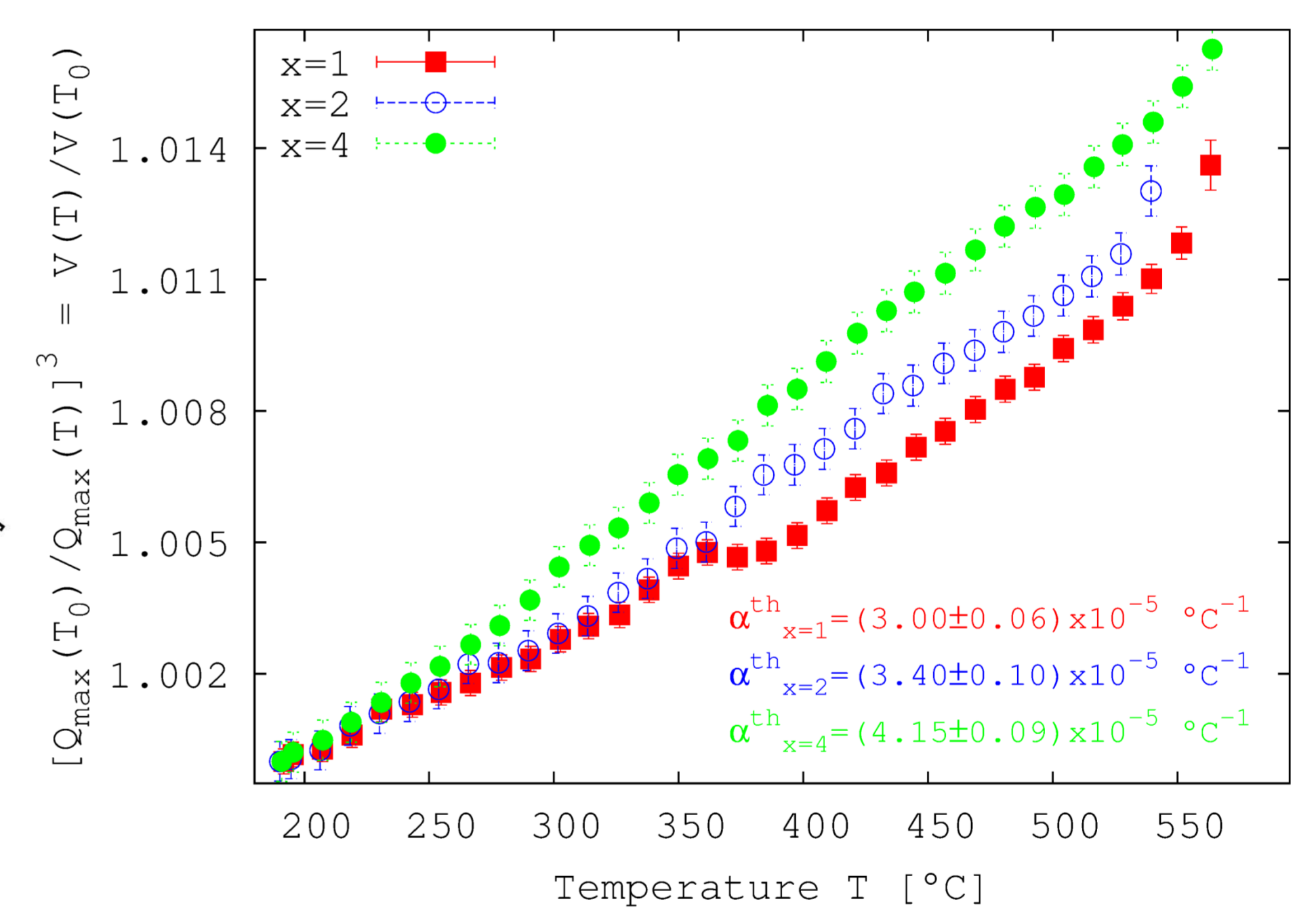


Series of XRD patterns acquired during constant-rate heating of the  $\text{Fe}_{61}\text{Co}_{10}\text{Zr}_5\text{B}_{20}\text{W}_1$  alloy.

Observed first crystallization temperatures 552°C ( $x=1$ ), 527°C ( $x=2$ ) and 564°C ( $x=4$ ) are in quite good accordance with calorimetric results presented in previous work [3] with an exception of the sample  $\text{Fe}_{61}\text{Co}_{12}\text{Zr}_5\text{W}_2\text{B}_{20}$ . This discrepancy is understandable in view of the fact, that in our case, the as-prepared  $\text{Fe}_{61}\text{Co}_{12}\text{Zr}_5\text{W}_2\text{B}_{20}$  sample is not fully amorphous and contains the subtle fraction of the crystalline  $\text{Fe}_{23}\text{B}_6$  phase which serves as crystalline seeds. XRD patterns taken at higher temperatures hints that the  $\text{Fe}_{23}\text{B}_6$  phase formed during the first crystallization is not stable and is transformed to other borides. Additionally, the phase analysis during second crystallization confirmed the formation of a cubic similar Fe phase and suggested the presence of the  $\text{Fe}_3\text{Zr}$  phase.



$D(r)$ s of as-prepared  $\text{Fe}_{61}\text{Co}_{(14-x)}\text{Zr}_5\text{B}_{20}\text{W}_x$  samples. Arrows sign changes in  $D(r)$ s. In the insert, the first maximum of  $D(r)$  is shown together with bond lengths and corresponding weights of atomic pairs for different W concentrations.



Relative volume changes of the  $\text{Fe}_{61}\text{Co}_{(14-x)}\text{Zr}_5\text{B}_{20}\text{W}_x$  ribbons during constant-rate heating.

## Acknowledgement

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