ELSEVIER

Journal of Alloys and Compounds 378 (2004) 242–247

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Structural investigations of submicrocrystalline metals obtained by high-pressure torsion deformation

R. Kužel [a,*], Z. Matěj [a], V. Cherkaska [a], J. Pešička [b], J. Čížek [c], I. Procházka [c], R.K. Islamgaliev [d]

[a] *Department of Electronic Structures, Faculty of Mathematics and Physics, Charles University, 121 16 Praha 2, Ke Karlovu 5, Czech Republic*
[b] *Department of Metal Physics, Faculty of Mathematics and Physics, Charles University, 121 16 Praha 2, Ke Karlovu 5, Czech Republic*
[c] *Department of Low Temperature Physics, Faculty of Mathematics and Physics, Charles University, 121 16 Praha 2, Ke Karlovu 5, Czech Republic*
[d] *Institute of Physics of Advanced Materials, Ufa State Aviation Technical University, Ufa, Russia*

Received 30 September 2003; accepted 15 December 2003

Abstract

Different samples prepared by high-pressure torsion deformation (Cu, Cu with addition of different amounts of Al_2O_3, Fe, Mg and Mg with 10 wt.% Gd) were investigated by X-ray powder diffraction (PXRD), positron lifetime spectroscopy (PL) and transmission electron microscopy (TEM). Conventional PXRD studies were carried out in order to determine lattice parameters, texture coefficients and especially crystallite size and microstrain (and dislocation densities). In simplified analysis, the profiles were analyzed in terms of the modified Williamson–Hall (WH) plots and more sophisticated analysis was performed by total powder diffraction pattern fitting. Small grains of the order of 50–300 nm and dislocation densities within the range of $1 \times 10^{13}\,m^{-2}$ up to $1 \times 10^{15}\,m^{-2}$ were determined. Observed line broadening anisotropy could be explained well for all the materials by the dislocation-induced line broadening and elastic anisotropy. Positron lifetime spectra have shown two major components—from positrons trapped at dislocations inside the distorted regions and the one attributed to positrons trapped in microvoids with the size of 4–5 vacancies. The values of crystallite size and dislocation density agree quite well with the estimations made from TEM. It was found that the addition of more than 0.5 wt.% Al_2O_3 prevents grain growth and keeps the dislocation density high up to about 400 °C. The amount of 0.3 wt.% is insufficient for that and significant grain growth is observed at about 200 °C.

Keywords: Metals; X-ray diffraction, dislocations, TEM; Positron spectroscopies

1. Introduction

Severe plastic deformation is an effective tool for production of compact submicrocrystalline samples. The materials are also often called ultra-fine grained (UFG). High-pressure torsion deformation is one possible way of the technique [1,2]. The specific structure of UFG materials leads to a number of unusual physical and mechanical properties. In particular, the UFG materials exhibit anomalous high diffusion activity [3], unusual changes in Curie temperature, saturation magnetization and elastic properties [4]. Moreover, the UFG materials are characterized by combination of the high strength and the ductility [1,5]. These advantageous mechanical properties make the UFG materials highly attractive for further industrial applications.

In the present study, selected samples of Cu, Cu with addition of different amount of Al_2O_3, Fe, Mg and Mg with 10 wt.% Gd prepared by high-pressure torsion deformation under 6 GPa were investigated by X-ray powder diffraction (PXRD), positron lifetime spectroscopy (PL) and transmission electron microscopy (TEM) and preliminary results are reported. Main attention is given to conventional powder XRD studies.

2. Experimental details

X-ray powder diffraction measurements were performed with the aid of XRD7 and HZG4 (Seifert-FPM) powder diffractometers using Cu Kα radiation filtered with a nickel foil and Soller slits placed in the diffracted beam. XRD profiles were fitted with the Pearson VII functions. The correction for instrumental broadening was performed with the aid of NIST LaB_6 standard and the Voigt function method.

* Corresponding author. Tel.: +420-221911394; fax: +420-224911061.
E-mail address: kuzel@karlov.mff.cuni.cz (R. Kužel).

0925-8388/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2003.12.048

Lattice parameters were determined in terms of the Cohen–Wagner plot and preferred orientation characterized simply by the Harris texture indices. Different methods of diffraction line profile analysis were applied. In simplified analysis, the line broadening was analyzed using integral breadths and half-widths (FWHM) in terms of the modified Williamson–Hall (WH) plots [6]. More sophisticated analysis was then performed by the total powder diffraction pattern fitting as proposed by Ungar et al. [7] and Scardi and Leoni [8].

TEM was performed for the high-pressure torsion deformed Fe and Cu with addition of Al_2O_3 using a Jeol 2000FX analytical microscope operating at 200 kV. Small disks (3 mm diameter) were cut out of the materials and these were mechanically polished down to a thickness of 0.1 mm and then thinned using a standard electrolytic double jet technique (Struers Tenupol). For Fe an electrolyte a solution of 6% perchloric acid in metanol was used at minus 33 °C and 25 V and in the case of Cu alloy an electrolyte solution of 20% nitric acid in metanol was used at minus 22 °C and 13 V.

A fast–fast PL spectrometer similar to that described in [9] was used for PL measurements. The spectrometer exhibits timing resolution 150 ps (FWHM ^{22}Na) at coincidence counting rate of 80 s^{-1}. We used a ^{22}Na positron source with activity of 1.5 MBq deposited on a mylar foil.

3. Results

Lattice parameters of all the samples investigated did not show significant deviations from standard stress free values given in the powder diffraction file PDF-2 [10]. This means both, the absence of impurities in the lattice and the absence of residual stresses. Different types of preferred orientation were observed. While the Fe samples where without any texture, in most of the Cu samples the (1 1 1) texture was observed and for Mg samples significant (0 0 1) texture was typical. For cubic phases the preferred grain orientation was characterized by the Harris texture index that is equal to unity in the absence of preferred orientation. For all the copper samples investigated the texture index was of about 2–2.5. Texture change $\langle 1\,1\,1\rangle \rightarrow \langle 1\,0\,0\rangle$ with annealing was observed for the Cu + 0.3% Al_2O_3 sample in the range between 160 and 220 °C. However, this was also connected with significant grain growth. The texture of hexagonal magnesium was evaluated by the empirical formula $I = I^{rand} \exp(-D \sin^2\psi)$, where D is the coefficient related to the degree of preferred orientation and ψ is the angle between the c-axis (texture direction) and particular reflecting plane normal. Observed D-values were about 5 and 2 for the Mg and Mg + Gd samples, respectively. In all cases, the exponential dependence described the texture function very well.

Line broadening analysis of the samples indicated significant differences between samples. However, general features could be found as well. Although, these materials had small grains in the order of 50–300 nm, the main reason for line broadening are dislocations. All the methods used gave reasonable dislocation densities within the range of 10^{14}–10^{15} m^{-2}. Different materials showed different line broadening anisotropy in dependence of elastic anisotropy. An example can be seen in Fig. 1. Typical line broadening anisotropy of iron could well be fitted assuming the most common slip systems and edge and screw dislocations with the Burgers vector $\boldsymbol{b} \parallel \langle 1\,1\,1\rangle$. Similarly, the anisotropy could be fitted for the fcc copper samples assuming dislocations with the Burgers vector $\boldsymbol{b} \parallel \langle 1\,1\,0\rangle$ (Fig. 2).

Typical TEM micrograph of as-deformed iron is shown on Fig. 3. There is a typical substructure of material after severe deformation with high density of dislocations and

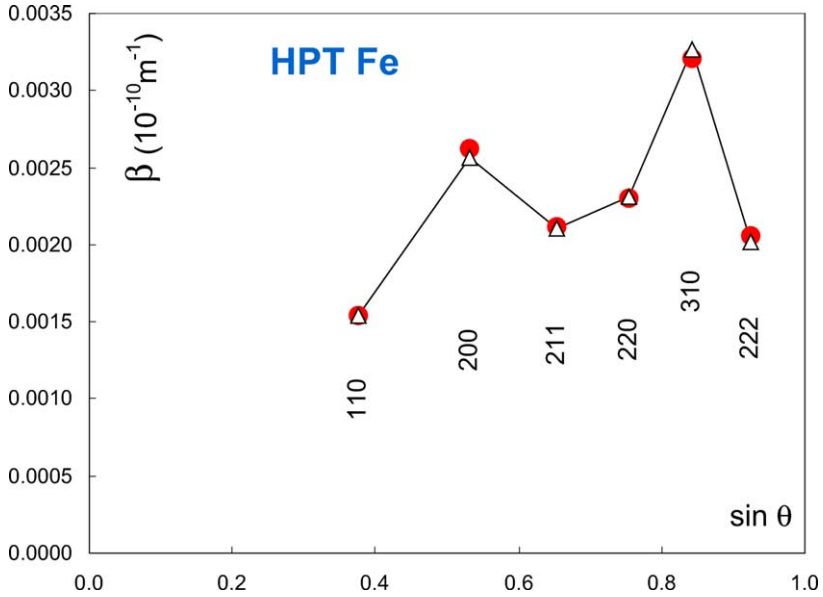


Fig. 1. Williamson–Hall plot β vs. sin θ for as-deformed iron showing typical line-broadening anisotropy (full dots—experimental values, triangles and line—values calculated assuming edge and screw dislocations with the Burgers vector $\boldsymbol{b} \parallel \langle 1\,1\,1\rangle$.

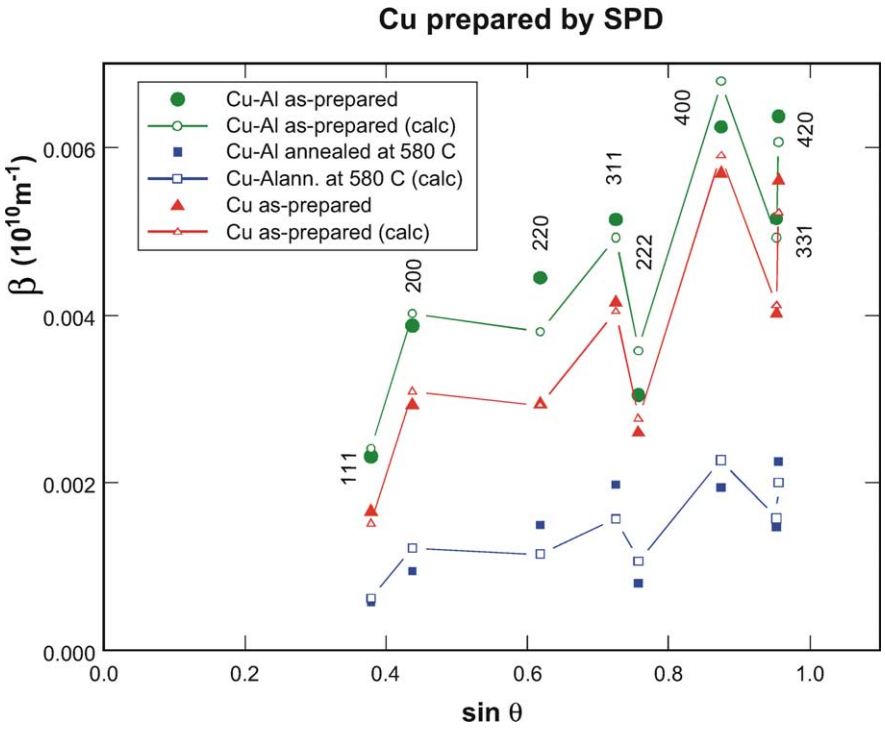
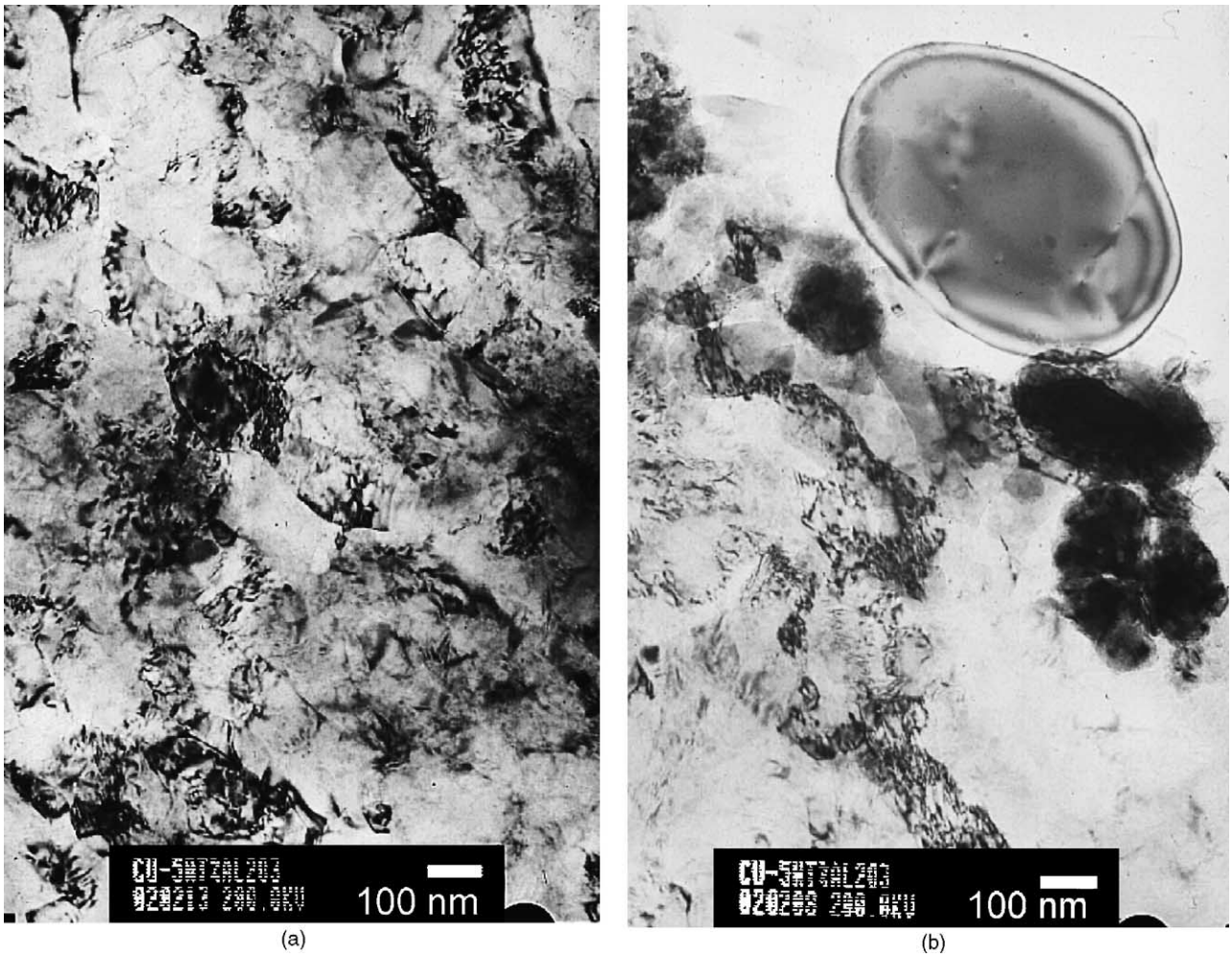


Fig. 2. Williamson–Hall plot β vs. sin θ for several samples as-deformed Cu (triangles), as-deformed Cu + 0.5 wt.% of Al_2O_3 (circles) and the latter sample annealed at 580 °C (squares) showing typical line-broadening anisotropy for copper (full symbols—experimental values, open symbols—values calculated assuming edge and screw dislocations with the Burgers vector $\boldsymbol{b} \parallel \langle 1\,1\,0 \rangle$.

small grains ranging in size from 200 to 500 nm. Inside of these grains are subgrains of about 100 nm large. However, the regions of grains without subgrain substructure were also observed. The values of crystallite size and dislocation density obtained from the Williamson–Hall plot are 95 nm and $4 \times 10^{14}\,m^{-2}$, respectively. The fine microstructure quite rapidly changes with isochronal annealing (30 min on each temperature from 100 °C). At 130 °C the dislocation density drops to half ($2 \times 10^{14}\,m^{-2}$) without change of crystallite size and after annealing at 190 °C further decrease to the value of $8 \times 10^{13}\,m^{-2}$ and increase of crystallite size to 150 nm were observed. Annealing experiments continue.

Fig. 3. Typical TEM micrograph of as-deformed iron.



(a) (b)

Fig. 4. Typical TEM micrograph of as-deformed Cu with 0.5 wt.% of Al_2O_3 (a) and selected area containing Al_2O_3 droplet (b).

Samples with different content of Al_2O_3 (0.3, 0.5 and 1.1%) were investigated. Crystallite size and dislocation densities of all the samples were 40–50 nm and 1×10^{15} m^{-2}, respectively. Results of study of the Cu + 0.5 wt.% of Al_2O_3 sample have been partially published [11]. Typical TEM pictures of Cu + 0.5 wt.% of Al_2O_3 sample are shown in Fig. 4a and b. On some of the TEM pictures Al_2O_3 droplets of the size of about 300–400 nm were found (Fig. 4b). It was found that the addition of at least 0.5 wt.% Al_2O_3 prevents grain growth and keeps the dislocation density high up to about 400 °C in comparison with pure copper where drop of dislocation density was observed already at 150 °C. However, the amount of 0.3 wt.% is insufficient for that and significant grain growth is observed at about 200 °C. This was clearly seen also on X-ray back reflection photos where discontinuous rings were detected.

Preliminary studies of magnesium samples have shown that in the Mg + 10% Gd sample lower broadening of (0 0 l) profiles indicate dominating dislocations with ⟨a⟩ Burgers vector in the direction [2 $\bar{1}$ $\bar{1}$ 0]. No significant broadening for pure Mg sample was detected so that the dislocation density is of the order of 1×10^{13} m^{-2} or less.

As even the modified WH method suffers from principle limitations, more sophisticated evaluation with the aid of full pattern or multiple profile fitting was performed using the programs MWP-fit [7] and PM2000 [8]. The fits were usually good (Fig. 5a) but not perfect (Fig. 5b). In case of the former program multiple fitting of Fourier coefficients was used. For this program the pure physical profile must be given for input. A number of deconvolution methods was tested for separation of instrumental broadening. The best results and good agreement of reconvoluted profiles with the experimental ones were obtained for modified Kojdecki regularization algorithm [12]. The principle problem of the dislocation density determination is correct evaluation of the correlation factor of dislocation arrangement (cut-off radius) that is highly correlated with the dislocation density. This factor is related to the profile shape but the sensitivity is not very high.

PL spectra have shown usually three major components—component with lifetime well below 100 ps can be obvi-

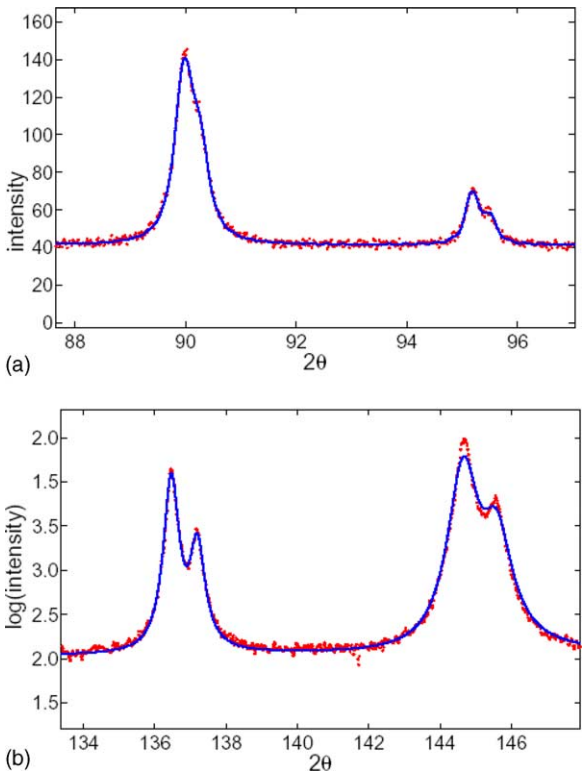


Fig. 5. Two segments of powder diffraction pattern for Cu sample annealed at 220 °C (311 and 222 peaks) (a) and sample annealed at 520 °C (331 and 420 peaks) (b).

ously attributed to free positrons. Relative intensity of this component is very small for most of the as-deformed samples. It clearly indicates that majority of positrons annihilate from trapped states at defects. In some cases, e.g. UFG Cu + 0.5 wt.% Al_2O_3, the free positron component was not detected and saturated positron trapping at defects occurs. A decrease of defect density and grain growth with increasing temperature during isochronal annealing lead to rise of the intensity of the free positron component [13,14]. The second component is dominating and comes from positrons trapped at dislocations. For example, the lifetime of this component for UFG Cu and UFG Cu with Al_2O_3 corresponds to the lifetime of 164 ps of positrons trapped at Cu dislocations [13,15]. Dislocations are situated in distorted regions along GBs, while grain interiors are almost free of dislocations, for detailed discussion see [13]. Similar picture was found also in UFG Fe. On the other hand, UFG Mg and UFG Mg–10 wt.% Gd exhibit homogeneous distribution of dislocations throughout whole grains. The third component with the longest lifetime represents a contribution of positrons trapped at microvoids inside grains [13]. Using theoretical calculations in ref. [13], one obtains that size of the microvoids in the as-deformed UFG Cu specimen corresponds to five monovacancies. Larger microvoids (more than 10 vacancies) were found in UFG Fe. On the other hand, no microvoids were detected in UFG Mg and UFG Mg–10 wt.% Gd.

4. Conclusions

Three complementary techniques were used for characterization of submicrocrystalline metals prepared by high-pressure torsion deformation. The values of crystallite size obtained from XRD and grain size measured by TEM are in approximate agreement. As usual, the values from XRD are smaller (50–300 nm for XRD, the TEM estimations start at 100 nm and go up to 500 nm, depending on samples). This has several reasons. For example, there may be a difference between the grain and crystallite–coherent domain. Dislocation densities were determined mainly from XRD in the present study. They were within the range 10^{14}–10^{15} m^{-2}. It was found that the addition of more than 0.5 wt.% Al_2O_3 prevents grain growth and keeps the dislocation density high up to about 400 °C. The amount of 0.3 wt.% is insufficient for that and significant grain growth was observed at about 200 °C. Stability of the fine microstructure of pure metals is much lower for both Cu and Fe samples. The strain relaxation starts after annealing at about 130 °C and it is followed by grain growth (at about 200 °C). Positron lifetime spectroscopy results show the presence of inhomogeneous dislocation distribution for Cu and Fe samples. This indicates the necessity of development of more appropriate model for the XRD evaluation. From PL measurements also the presence of microvoids could be found—5 and 10 monovacancies for Cu and Fe, respectively.

Acknowledgements

This work was partially supported by the Grant Agency of the Czech Republic-Czech Science Foundation (contracts 106/01/D049 and 106/02/1521), the Ministry of Education, Youth and Sports of the Czech Republic (project COST OC523.50).

References

[1] R.Z. Valiev, Mat. Sci. Eng. A 234–236 (1997) 59.
[2] R.Z. Valiev, Nanostruct. Mater. 6 (1995) 173.
[3] R.Z. Valiev, R.S. Musalimov, N.K. Tsenev, Phys. Status Solidi (a) 115 (1989) 451.
[4] R.Z. Valiev, I.V. Alexandrov, R.K. Islamgaliev, in: G.M. Chow, N.I. Noskova (Eds.), Nanocrystalline Materials: Science and Technology, NATO ASI, Kluwer Publication, 1998, p. 121.
[5] R.Z. Valiev, R.K. Islamgaliev, in: A.K. Ghosh, T.R. Bieler, Superplasticity and Superplastic Forming 1998, The Minerals, Metals and Material Society, 1998, p. 117.
[6] R. Kužel, J. Čížek, I. Procházka, F. Chmelík, R.K. Islamgaliev, N.M. Amirkhanov, Mater. Sci. Forum 378–381 (2001) 463–468.
[7] T. Ungár, J. Gubicza, G. Ribárik, A. Borbély, J. Appl. Cryst. 34 (2001) 298–310.
[8] P. Scardi, M. Leoni, Acta Crystallogr. A58 (2002) 190–200.
[9] F. Bečvář, J. Čížek, L. Lešták, I. Novotný, I. Procházka, F. Šebesta, Nucl. Instr. Meth. A 443 (2000) 557.
[10] International Centre for Diffraction Data, PDF-2 database.
[11] J. Čížek, I. Procházka, R. Kužel, R.K. Islamgaliev, Monatshefte fur Chemie 133 (6) (2002) 873–887.

[12] M.A. Kojdecki, Mater. Sci. Forum 378–381 (2001) 12–17.
[13] J. Čížek, I. Procházka, M. Cieslar, R. Kužel, J. Kuriplach, F. Chmelík, I. Stulíková, F. Bečvář, R.K. Islamgaliev, Phys. Rev. B 65 (2002) 094106.
[14] J. Čížek, I. Procházka, R. Kužel, M. Cieslar, R.K. Islamgaliev, J. Metastable Nanocryst. Mater. 17 (2003) 37.
[15] J. Čížek, I. Procházka, P. Vostrý, F. Chmelík, R.K. Islamgaliev, Acta Phys. Pol. A 95 (1999) 487.