Elsevier Editorial System(tm) for Materials Science and Engineering B

Manuscript Draft

Manuscript Number:

Title: Investigation of structural relaxation, crystallization process and magnetic properties of the Fe-Ni-Si-B-C amorphous alloy

Article Type: Research Paper

Section/Category:

Keywords: Metallic glasses, rapid-solidification, magnetic measurements, thermal analysis.

Corresponding Author: Mrs. Aleksandra Kalezic-Glisovic,

Corresponding Author's Institution: Technical faculty

First Author: Aleksandra Kalezic-Glisovic

Order of Authors: Aleksandra Kalezic-Glisovic; Aleksandra Kalezic-Glisovic

Manuscript Region of Origin:

Abstract:

Text Only

**Aleksandra Kalezić - Glišović**

**Joint Laboratory for Advanced Materials**

**of Serbian Academy of Sciences and Arts**

**- Section for Amorphous Systems -**

**Technical Faculty Čačak, Svetog Save 65, 32000 Čačak,**

**SERBIA**

**Tel. + 381 32 302 758, fax + 381 32 342 101,**

**e-mail: aleksandrakalezic@eunet.yu; akalezic@tfc.kg.ac.yu**

# Investigation of structural relaxation, crystallization process and magnetic properties of the Fe-Ni-Si-B-C amorphous alloy

**A. Kalezić-Glišović[1,*], L. Novaković[2], A. Maričić[1], D. Minić[3], N. Mitrović[1]**

[1] *Joint Laboratory for Advanced Materials of SASA, Section for Amorphous Systems Technical Faculty Čačak, Svetog Save 65, 32 000 Čačak, Serbia and Montenegro*
[2] *Faculty of Physics, Studentski trg 16, 11 000 Belgrade, Serbia and Montenegro*
[3] *Faculty of Physical Chemistry, Studentski trg 16, 11 000 Belgrade, Serbia and Montenegro*

**Abstract**

The differential scanning calorimetry method was used for investigating the crystallization process of the $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ amorphous alloy. It was shown that the examined alloy crystallizes in three stages. The first crystallization stage occurs at 799 K, the second at 820 K and the third at 888 K. Temperature dependence of the magnetic susceptibility relative change was investigated by the modified Faraday method in the temperature region from room temperature up to 900 K. It has been established that the Curie temperature is about 700 K for amorphous state. The magnetic susceptibility increases by 30 % after the first heating up to 710 K. During the second heating up to 840 K the alloy loses its ferromagnetic features in the temperature region from 710 K to 760 K, upon which it again regains the same. After the second heating magnetic susceptibility decreases by 23 % as compared to the amorphous starting value and by 53 % as compared to the value before the second heating. The crystallized alloy maintains ferromagnetic features in the whole temperature region during the heating up to 900 K.

**Key words:** Metallic glasses, rapid-solidification, magnetic measurements, thermal analysis.

*Corresponding author: Tel. +381 32 355 622; +381 32 302 758; Fax: +381 32 342 101
*E-mail*:aleksandrakalezic@eunet.yu (A.Kalezić-Glišović), nmitrov@tfc.kg.ac.yu (N. Mitrović)

## Introduction

The metallic glasses represent a novel class of metallic materials characterized by amorphous structure and metallic bond providing them with unique physical and mechanical properties that cannot be found either in pure metals or other amorphous materials [1]. It has been shown that it is a consequence of their microstructure with absence of long distance order atom arrangement [2]. The amorphous state of matter is, however, structurally and thermodynamically unstable and very susceptible to partial or complete crystallization during thermal treatment or nonisothermal compacting. The latter requires the knowledge of alloys stability in a wide range of temperature. Generally, the stability is a thermally activated process of transition from disordered amorphous structure to an ordered crystal structure. The requirements for the soft magnetic alloys with nonequilibrium structure produced by melt quenching technique involve the design of the proper chemical composition that provides improved levels of the properties, such as a high glass-forming ability, good casting properties for the alloy which in turn determine the surface quality and uniformity of the melt-spun ribbons, as well as an enhanced thermal stability of both magnetic properties and amorphous structure [3]. A lot of papers have been dedicated to amorphous alloys ferromagnetism [4-9], comprising the results of investigation of magnetic properties for alloys of different content. Generally an amorphous structure is assumed to introduce fluctuations in exchange interactions, which influence magnetic behaviour. It has been shown that exchange interactions of 3d electrons of neighbour atoms are accountable for ferromagnetism of ferrous group metal based amorphous alloys, as well as of crystal alloys, while magnetic properties distinctiveness of amorphous metal alloys is generally determined by locally changeable surroundings of each transition metal (TM) atom [9].

Atomic disorder and defects of different levels play the main role in magnetic properties determination. The results of various elements impact on magnetic moment $\vec{M}$ and Curie temperature $T_C$ of amorphous metal alloys are very inconsistent [10-13]. Magnetization $\vec{J}$ and Curie temperature $T_C$ decrease during the transition from crystal to amorphous state with all ferrous group metal based amorphous alloys. Magnetic moment in TM amorphous alloys is determined by the number of electrons introduced into TM 3d zone [10]. The aim of this paper is to present the preliminary results of investigation of the changes in magnetic susceptibility and Curie temperature during the transition from amorphous to crystal state of $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ amorphous alloy. The rationale of this study is the composition of Fe-based soft magnetic alloy with significant decrease in atomic percentage of the metalloids (less than 10 at. %).

**Experimental**

Ribbon shaped samples of $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ amorphous alloy were obtained using the standard procedure of rapid quenching of the melt on a rotating disc (melt-spinning). The obtained ribbon was 2 cm wide and 35 μm thick. The crystallization process was investigated in a nitrogen atmosphere by the differential scanning calorimetry (DSC) method using SHIMADZU DSC-50 analyzer in the temperature region from room temperature to 1000 K. X-ray diffraction investigations were performed using Cu-$K_\alpha$ radiation lines ($\lambda$=0.154178 nm) on a Phillips PW1710 device. Measurements of the temperature dependence of electrical resistivity were performed in a hydrogen flow by the four points method. Temperature dependence of the relative magnetic susceptibility was investigated by the modified Faraday method in the temperature region from room temperature up to 900 K, in argon atmosphere. The sample of 44 mg is introduced into magnetic field by glass sample holder at the level of upper base of vertically positioned solenoid where magnetic field gradient is $\Delta H/\Delta z = 10^6$ A/m/m (1.26 mT/mm). After that, the relative change in magnetic susceptibility through three heating cycles is monitored in the temperature region from room temperature to 900 K.

**Results and discussion**

**a) Investigation of the crystallization process**

DSC thermogram (Fig. 1) shows Curie temperature $T_C$ at 700 K as well as the glass transition process at about 720 K followed by a super-cooled liquid region before an exothermic reaction. The reaction is the indicator of amorphous alloy crystallization process occurring in three separated stages with temperature peaks of $T_{k1}$=799 K, $T_{k2}$=820 K and $T_{k3}$=890 K. Enthalpies of corresponding steps determined from area maxima are $H_1$=55 J/g, $H_2$=11 J/g and $H_3$=19.2 J/g, respectively.

For better understanding of the crystallization mechanism, the analysis of X-ray patterns of the original sample (Fig. 2a) and the sample heated at temperature just above the crystallization peak in DSC scan was conducted. (Fig.2b). The starting alloys exhibitted a diffuse halo peak charcteristical for amorphous structure with the signs of crystallization probably the due to the presence of small amount of metalloids (Si, B and C). The sample heated above crystalization temperature has no signs of amorphous structure and consists of different phases: α-Fe(110) with traces of $Fe_2B$ (221) (peak 1), FeB (202) (peak 2) and $Fe_5Si_3$ (220) (peak 3).

**b) The analysis of thermomagnetic measurements results**

Thermomagnetic measurements were performed by Faraday method, which is based on the inhomogeneous magnetic field effect on magnetic material. The condition that the value of magnetic field intensity H multiplied by its change along the vertical axis is constant has been fulfilled by special construction of vertically positioned solenoid. Magnetic field intensity H at the sample positioning spot was 7 kA/m.

During the first and second heating, the decrease in magnetic susceptibility in temperature region from 690 K to 710 K is the result of getting closer to Curie temperature ($T_C$) of amorphous alloy (Fig.3). After the first heating in amorphous state temperature region up to 710 K (see DSC curve on Fig. 1) and upon cooling to room temperature, magnetic susceptibility increases by 30 % (Fig. 3b). Magnetic susceptibility increase upon the first heating is caused by structural relaxation of amorphous structure during the first heating.

Within the process in concern, internal strains and free volume are reduced in starting material. These changes are accompanied by subtle interatomic movements, bringing about the changes in electron structure. This leads to an increase in the number of electrons with unpaired spin in the direction of outer magnetic field, as well as to the decrease in number of electrons with the spin of reversed direction than that of the field, which causes an increase in magnetic susceptibility upon cooling. At the same time strains and free volume decrease during structural relaxation enables greater mobility of magnetic domains walls, which further contributes to magnetic susceptibility increase.

During the second heating (Fig. 3b) in temperature region from 710 K to 760 K the alloy loses its ferromagnetic features. With further heating up to 840 K magnetic susceptibility starts rising and the alloy regains its ferromagnetic features, since the crystallization process starts at about 800 K (see DSC curve on Fig. 1). After the second heating up to 840 K, magnetic susceptibility decreases by 23 % (Fig. 3b) as compared to the value in amorphous state ($\chi_{300\ K}$) and by 53 % as compared to the value in relaxed state after first heating. During the second (Fig. 3a) and the third heating (Fig. 3b) above crystallization temperature, alloy maintains its ferromagnetic features in the whole temperature region, whereas the maximum change in magnetic susceptibility occurs at about 460 K as a consequence of further phase transformation crystallized alloy.

**c) The analysis of electrical resistivity measurements**

Fig. 4a graph shows temperature dependence of the electrical resistivity of the investigated amorphous alloy. The obtained graph clearly shows that each crystallization stage is followed by electrical resistivity decrease. The differentiation of obtained correlation ρ(T) (Fig. 4b) shows that the maximum in resistivity temperature coefficient occurs at about 700 K when the effects of conductive electrons scatering on magnons disappeared [14,15]. At that temperature the amorphous alloy loses its ferromagnetic features ($T_C$), which is in excellent correlation with the thermomagnetic measurements results (Fig. 3a).

**Conclusion**

This paper give the analysis of the correlation between processes of structural relaxation and crystallization and relative changes in magnetic susceptibility of the $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ amorphous alloy. It was shown that the crystallization process occurs in three stages with crystallization peak temperatures of the first stage 799 K, of the second stage 820 K and of the third stage 888 K. The temperature dependence of magnetic susceptibility was investigated in three heating cycles in temperature region from room temperature to 900 K. It was shown that the amorphous alloy loses its ferromagnetic features at the temperature of about 700 K ($T_C$), which is in accordance with the results obtained from temperature dependence of specific electric resistivity. Upon the first heating up to 710 K, magnetic susceptibility of the examined alloy increases by 30 % as compared to the start value before the first heating. During the second heating up to 840 K, in temperature region from 710 K to 760 K, the alloy loses its ferromagnetic features, meaning that it maintains amorphous structure in that temperature region. After that, magnetic susceptibility rises during further heating and the alloy regains its ferromagnetic features, since the crystallization process starts. Upon the second heating magnetic susceptibility decreases by 23 % as compared to the start value before the first heating, and by 53 % as compared to the value before the second heating. During the third heating up to 900 K the alloy maintains its ferromagnetic features in the whole temperature region as it has completely crystallized.

**References**

[1] D.S. Jong, J.H. Kim, E. Fleury, W.T. Kim, D.H. Kim, J. Alloys and Compounds, 389 (2005) 159.

[2] D.R. Santos, D.S. Santos, Materials Research, 4 (2001) 47.

[3] K.G.Raval, K.N.Lad, A.Pratap, A.M. Awasthi, S. Bhardwaj, Thermochimica Acta 425 (2005) 47.

[4] J.A.Kunickij, J.I.Kupina, V.A.Mohort, A.V.Nemirovskij, NTUU "KPI", (1994) 116.

[5] H.Hilzinger, J. Magn. and Magn. Mater., 83 (1-3) (1990) 370.

[6] A.P.Spak, V.L.Karbovskij, A.N.Jaresko, Metalofizika i noveisie tehnologii, 16 (3) (1994) 32.

[7] O.V.Gregorieva, M.V.Belous, A.M.Lehnik, S.I.Sidorenko, L.D.Demčenko, Metalofizika i noveisie tehnologii, 26 (9) (2004) 1163.

[8] A.P.Spak, J.A.Kunickij, Z.A.Samoilenko, *Samoorganizacija strukturi v materialah različnoj prirodi*, Kiev, Akademperiodika, (2002) 72-74.

[9] K.G. Efthimiadis, G. Stergioudus, S.C. Chadjivasiliou, I.A. Tsoukalas, Cryst. Res. Technol. 37 (2002) 827

[10] A.P.Spak, J.A.Kunickij, V.I.Lisov, *Klasternie i nanostrukturnie materiali*, Kiev, Akademperiodika, (2002).

[11] K.Suzuki, H.Fudzimori, K.Yasamoto, *Amorfnye metally*, Metallurgiya, Moskva, 1987.

[12] V.E.Egoruskin, N.V.Melnikova, Metalofizika, T.10(1) (1988) 81.

[13] A.P. Spak., V.L. Karbovskij, A.V. Bliznij, *Bliznij poredak i osobennosti elektronnoj strukturi v amorfnih metalliceskih splavah na osnove 3d-metallov*, KNMF, (1994) 44.

[14] G.Bohnke, S.N.Kaul, W.Kettler, M.Rosenberg, Solid State Commun. 48 (9) (1983) 743.

[15] I.Balberg, J.S.Helman, Phys. Rev. B 18 (1) (1978) 303.

**Figure Captions:**

Fig. 1. DSC thermogram of $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ amorphous alloy obtained at heating rate of 20 K/min.

Fig.2 X-ray diffractograms: a) starting sample, b) sample heated up to 870 K in hydrogen atmosphere.

Fig.3. Temperature dependence of relative magnetic susceptibility of $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$: a) amorphous alloy (1) and crystallized alloy (2); b) (1) the first heating up to 710 K, (2) the second heating up to 840 K and (3) the third heating up to 900 K in argon atmosphere.

Fig.4. Temperature dependence of: a) electrical resistivity, b) the first derivative of electrical resistivity of $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ amorphous alloy.

Figure 1.

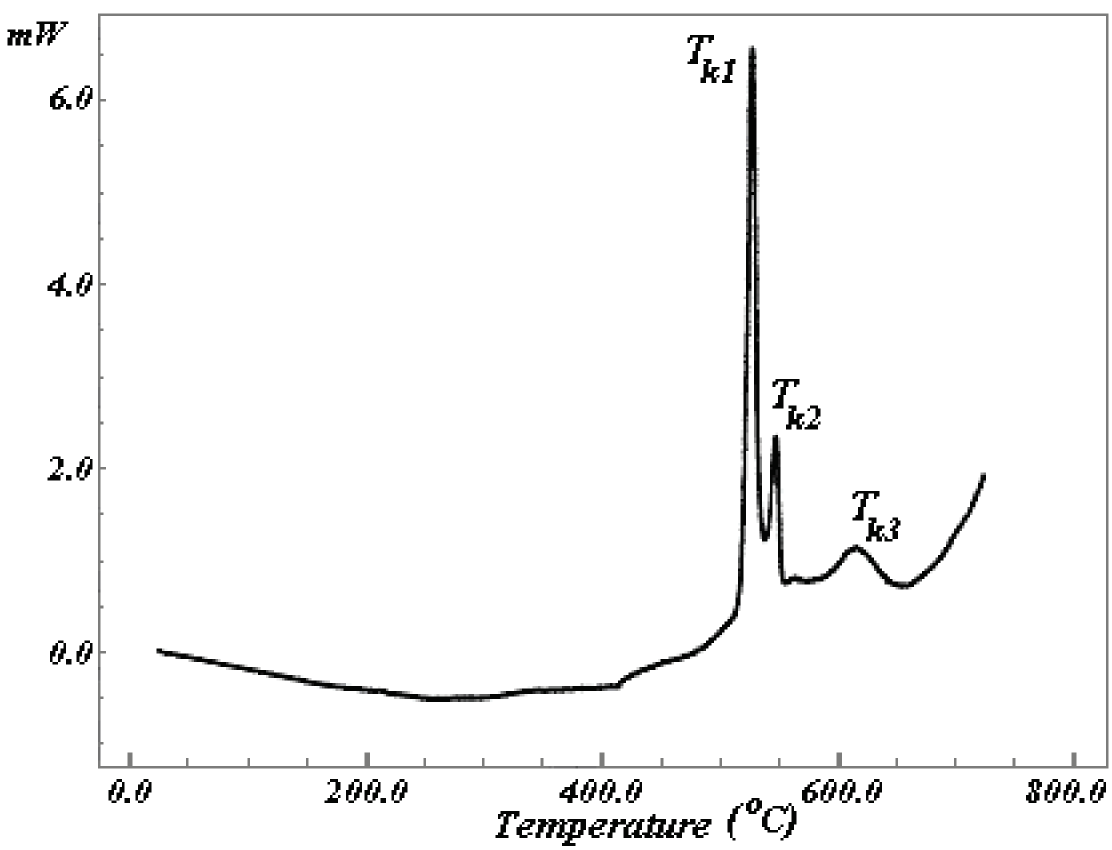

Figure 2a.
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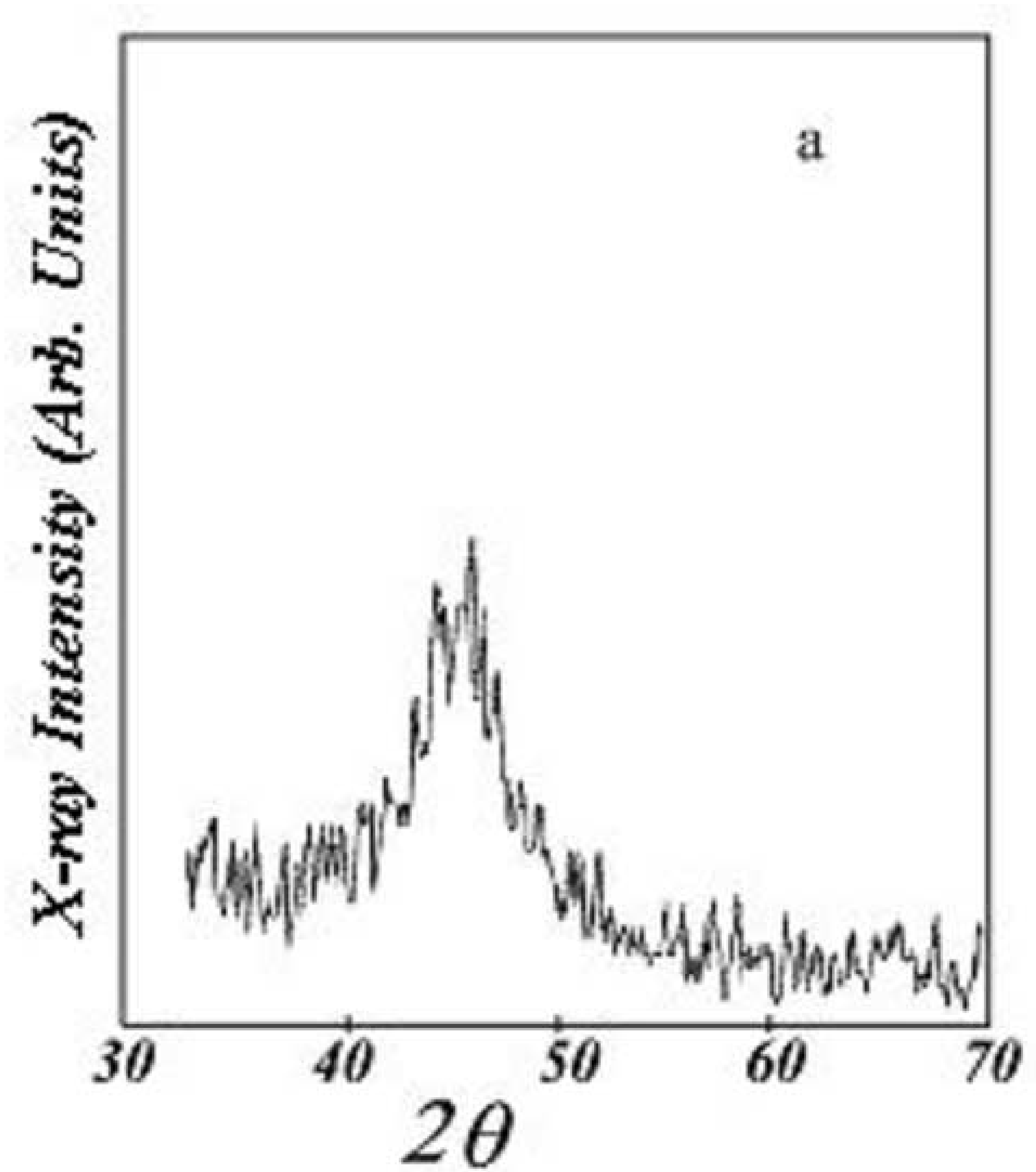

Figure 2b.
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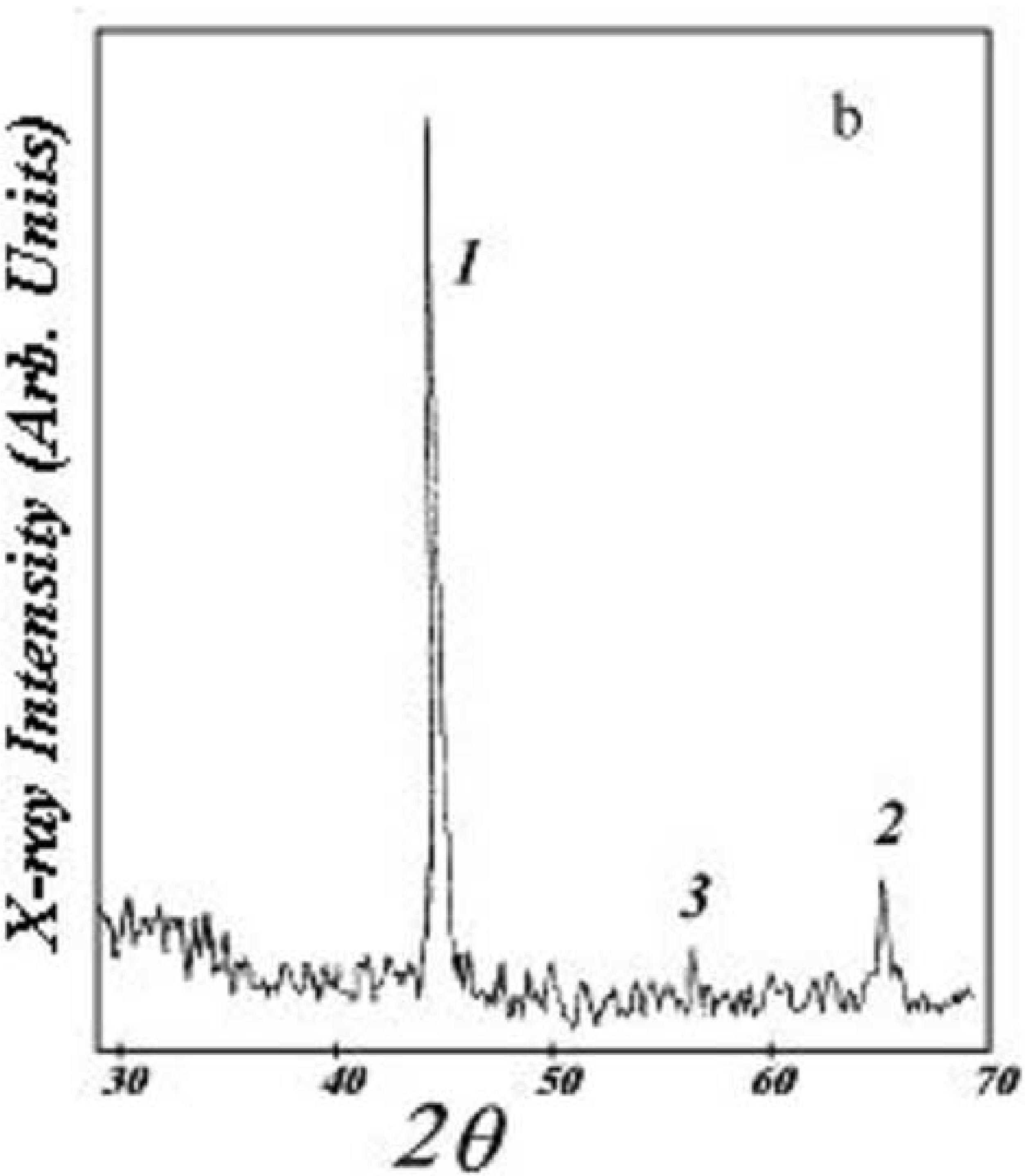

Figure 3a.
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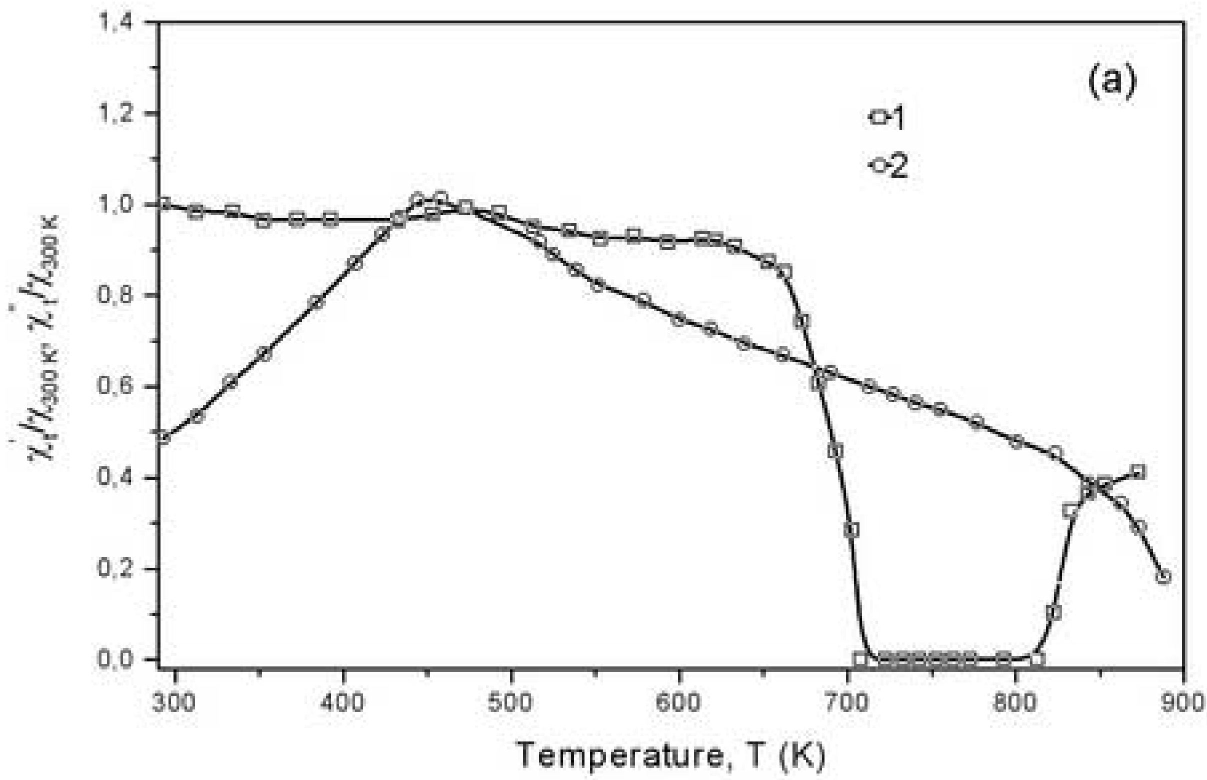

**Figure 3b.**

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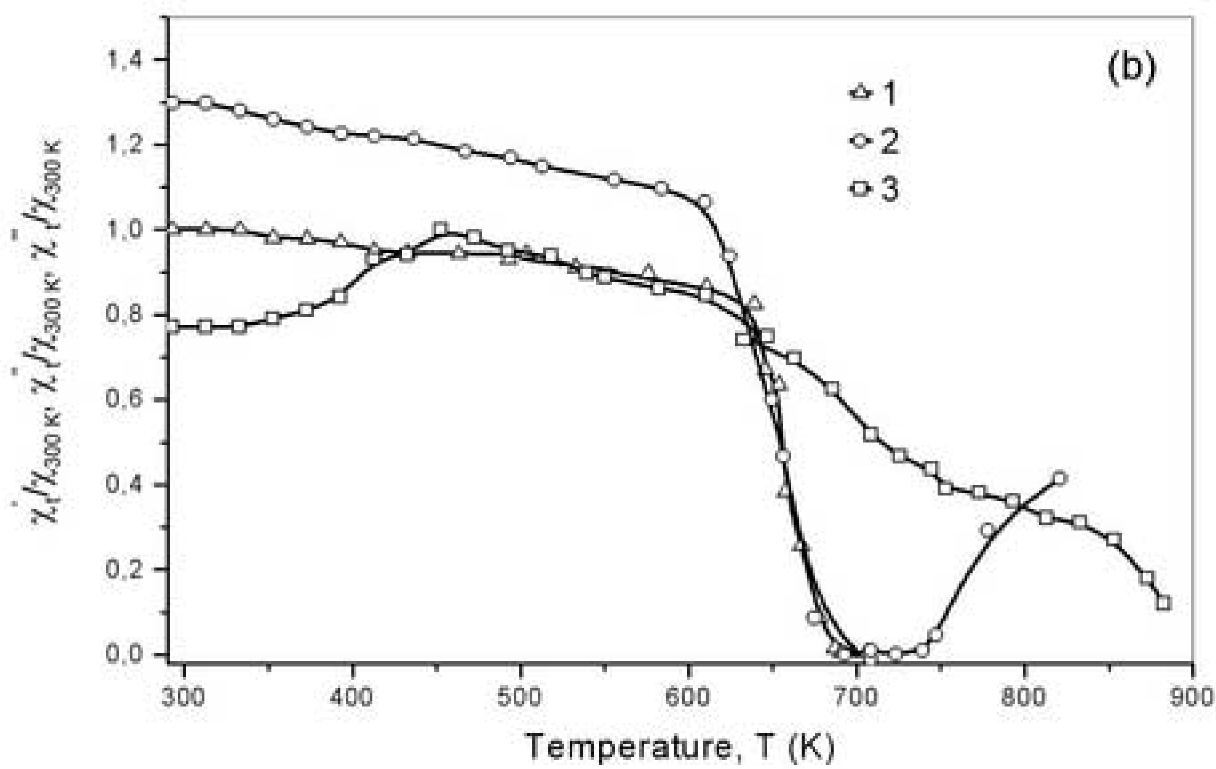

Figure 4.
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