Investigation of the Magnetocaloric Effect of Cooling

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**Abstract.** The article considered the prospects of utilizing phase transitions to achieve a wider temperature working interval for FEM. The analysis of experimental data has shown that the data obtained for adiabatic temperature change and isothermal entropy change are not always reliable. Often, they are accepted with significant errors for the determination and measurement of the magnetocaloric effect at the change of magnetic field in manganates of different compositions. The paper also discusses schemes for studying the magnetocaloric effect in magnetic materials. In these schemes, the working body is demagnetized in the absence of a magnetic field, resulting in a decrease in its temperature as heat is transferred from the heat source—the cooled body. Once thermal equilibrium is established, the cycle repeats. In this process, the FEM enables the operation of the magneto-heat pump, which effectively “pumps” heat from the cooled body.

**Keywords:** Magnetocaloric effect, isothermal, refrigerants, magnetic cooling, phase transitions, platinum-platinum rhodium, diffractogram, crystalline, phosphorus concentration

# INTRODUCTION

The design of a compact, environmentally safe, energy-efficient, and highly reliable refrigerator operating in the room temperature range is extremely important nowadays. It is caused by many serious claims about the currently operating cooling systems. It is well-known, in particular, that the currently used cooling systems may leak working gases (refrigerants), causing serious environmental problems such as ozone depletion and global warming. Of the various alternative technologies that could be used in refrigeration devices, magnetic cooling technology based on the magnetocaloric effect (MCE) is attracting increasing attention from researchers all over the world [1, 2].

Recently, perovskite manganates have been intensively studied, which, first, allow us to vary the temperature of phase transitions in a wide temperature range and, thus, to realize a wider temperature operating interval of FEM, and, second, are economically advantageous [1, 3]. There are many works devoted to the study of manganates of different compositions and FEM in them, but there is practically no information about adiabatic temperature measurement by direct method when the magnetic field changes [1, 4]. In [3] it was noted that significant FEM is observed in WA-Ca-MP Oz manganates, but their Curie temperature is much lower than room temperature, which limits the possibility of their application in cooling devices operating at room temperatures.

# MATERIALS AND METHODS

Experimental methods. Polycrystalline powders of solid solutions of the MnAs1-yPy system were synthesized by the fusion of solid-phase reactions of initial components in vacuum-quartz ampoules in a single-zone resistance furnace [5]. The synthesis was carried out by a slow stepwise increase in temperature to 1173K, followed by cooling of the ampoule to room temperature. The temperature was monitored with a platinum-platinum-rhodium thermocouple relative to the melting ice temperature. The error of temperature determination was ± 5K. The working zone length of the furnace was about 0.15 m.

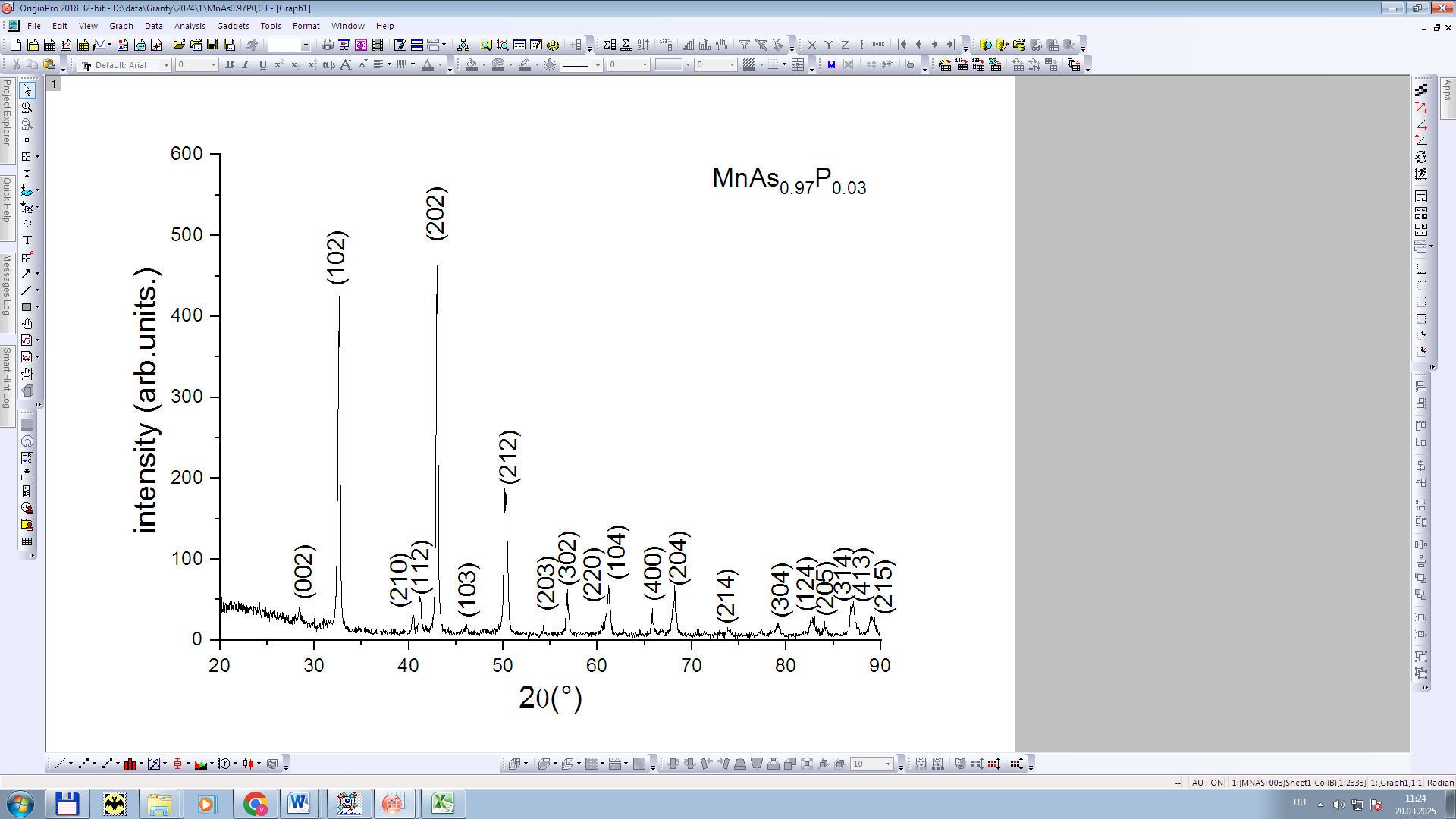
The initial components of the synthesis had the following characteristics in terms of purity: manganese of 99.98% purity and arsenic and phosphorus of 99.99% purity. Quartz ampoules were preliminarily etched with concentrated nitric acid, after which they were repeatedly washed with distilled water and dried in a muffle furnace. When determining the mass of samples and suspensions, precision analytical scales Sartorius CP124S were used, allowing weighing with an absolute error of 10-4 g. Ampoules with suspensions prepared in this way were evacuated to a pressure of 10-2 Pa and sealed [7, 9].

The following temperature regime of synthesis was used:

1. The oven temperature was raised to 873 K and held at this temperature for 12 hours.

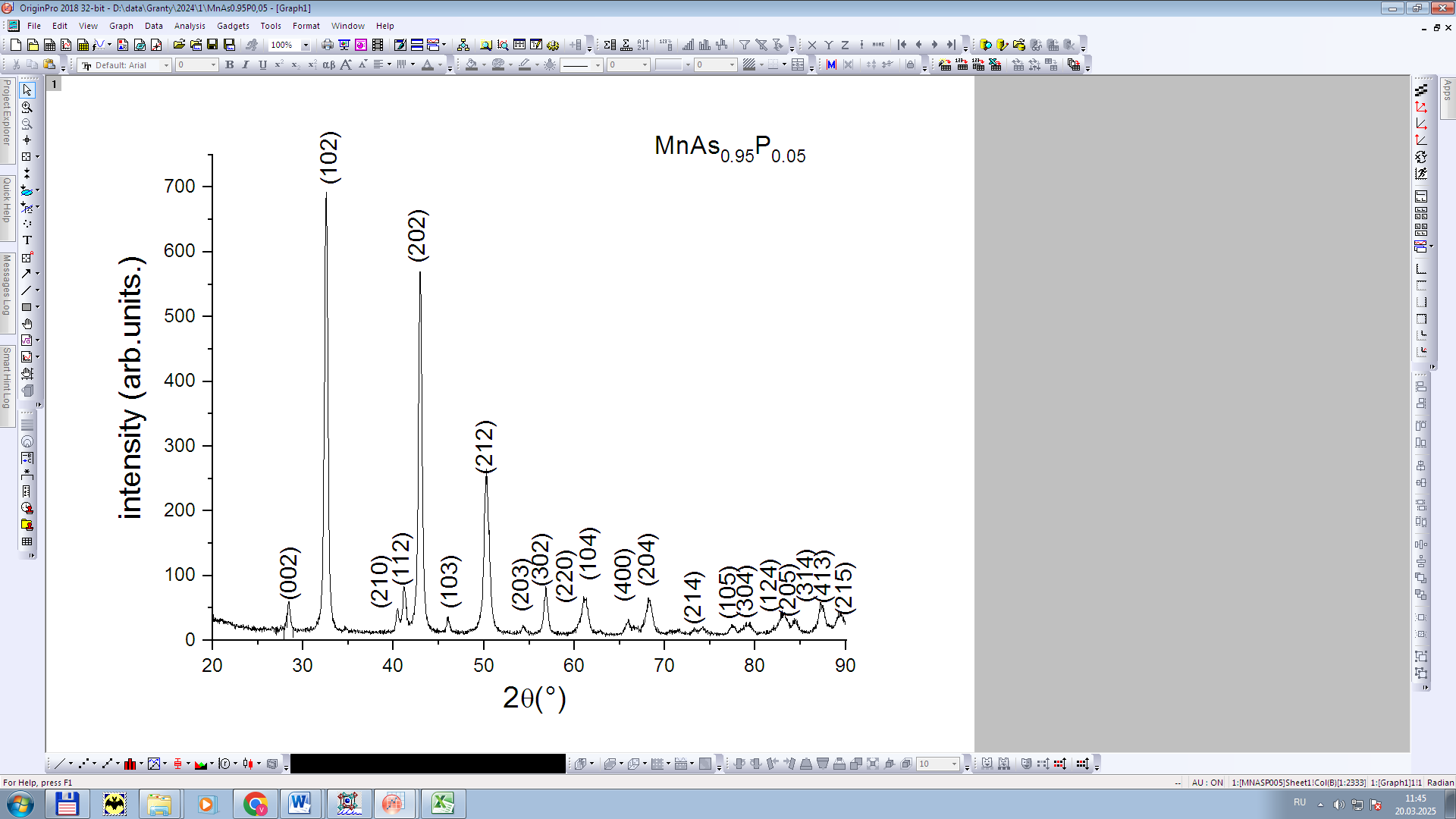
2. Further increase the temperature to 1173 K, holding at this temperature for 24 hours.

Cooling of the ampoule together with the furnace to room temperature.

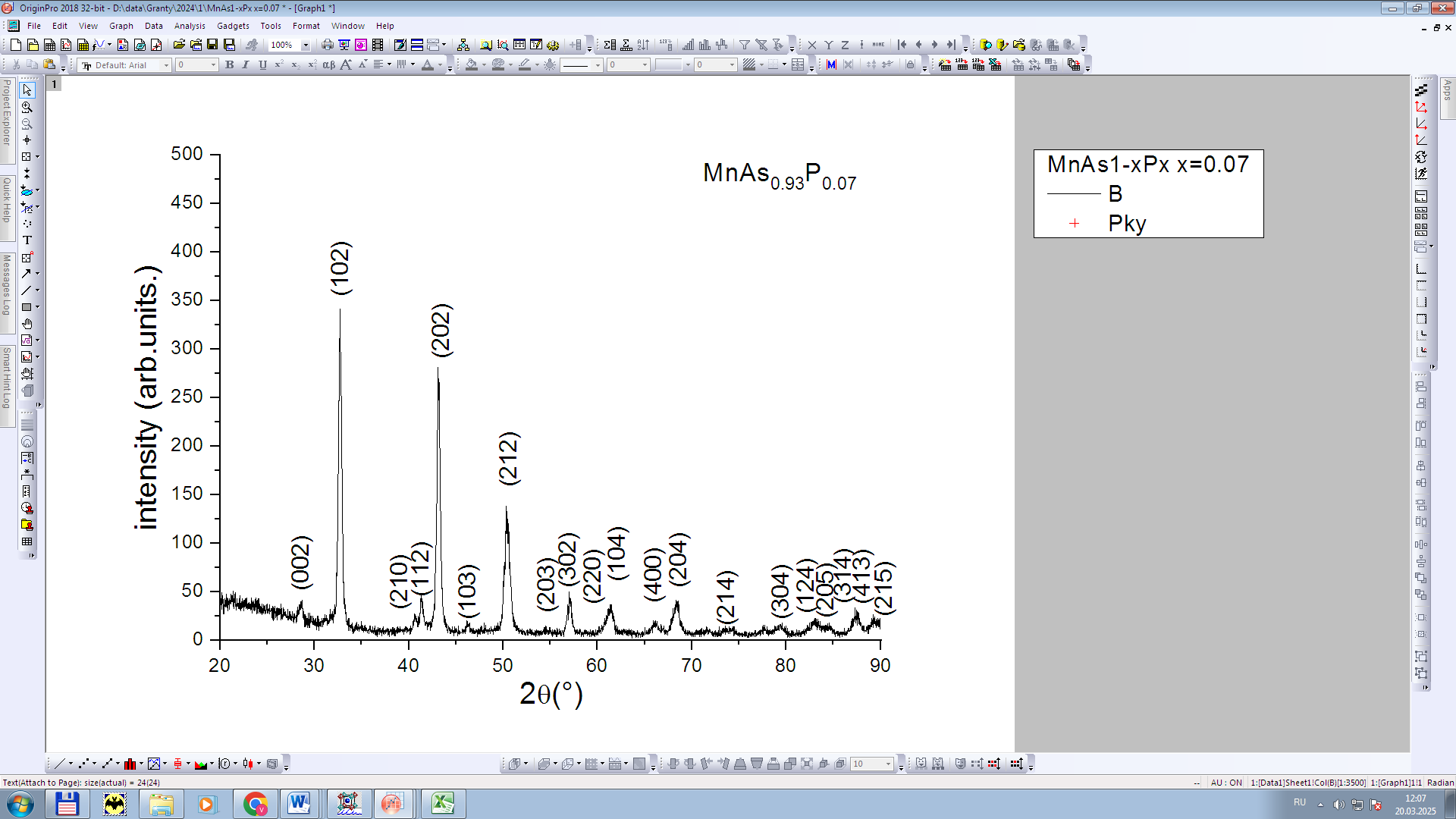


**FIGURE 1.** Diffractogram of MnAs0.97P0.03 solid solution

The phase composition and unit cell parameters of the synthesized compositions were determined using X-ray diffractograms (see Fig. 1) in CuKα-radiation obtained at room temperature [6, 8].



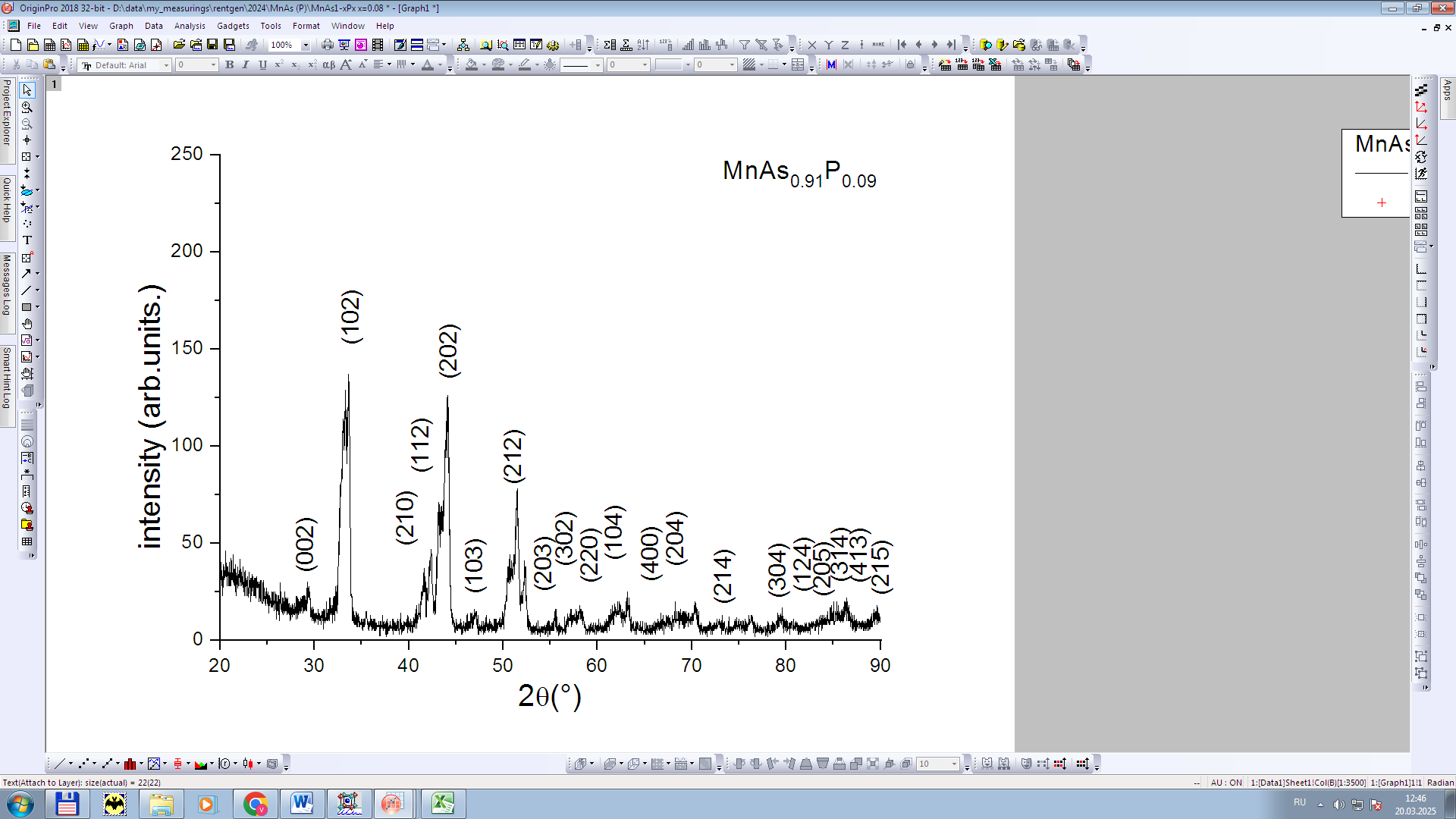
**FIGURE 2.** The diffractogram of MnAs0.95P0.05 solid solution



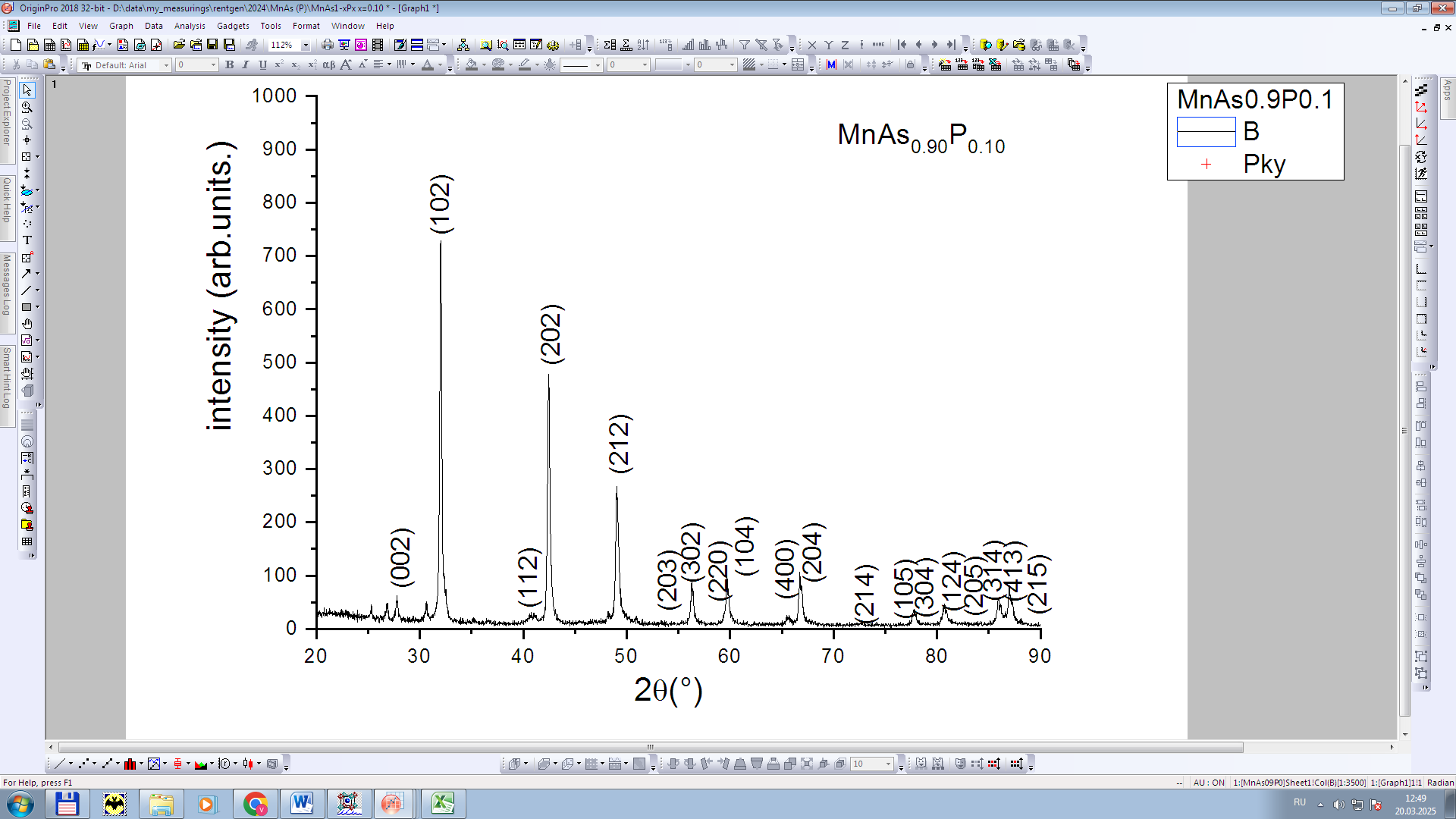
**FIGURE 3.** Represents X-ray diffraction patterns of Mn1-x Cox NiGe solid solution powders in the angle range 20° ≤ 2Θ ≤ 90° taken at room temperature

# RESULTS

It was found that MnAs1-yPy (0.03≤x<0.10) samples at room temperature have an orthorhombic structure *B*31 [7, 11].



**FIGURE 4.** Diffractogram of MnAs0.91 P0.09 alloy



**FIGURE 5.** Diffractogram of MnAs0.91P0.09 alloy

As can be seen from the corresponding X-ray radiographs, MnAs1-y Py alloys at y<0.1 are single-phase with orthorhombic structure B31, and at y=0.1, two-phase.

The numerical values of parameters a, b, c, axial ratio c/a, and unit cell volume V of MnAs1-y Py solid solutions are given in Table 1. [7].

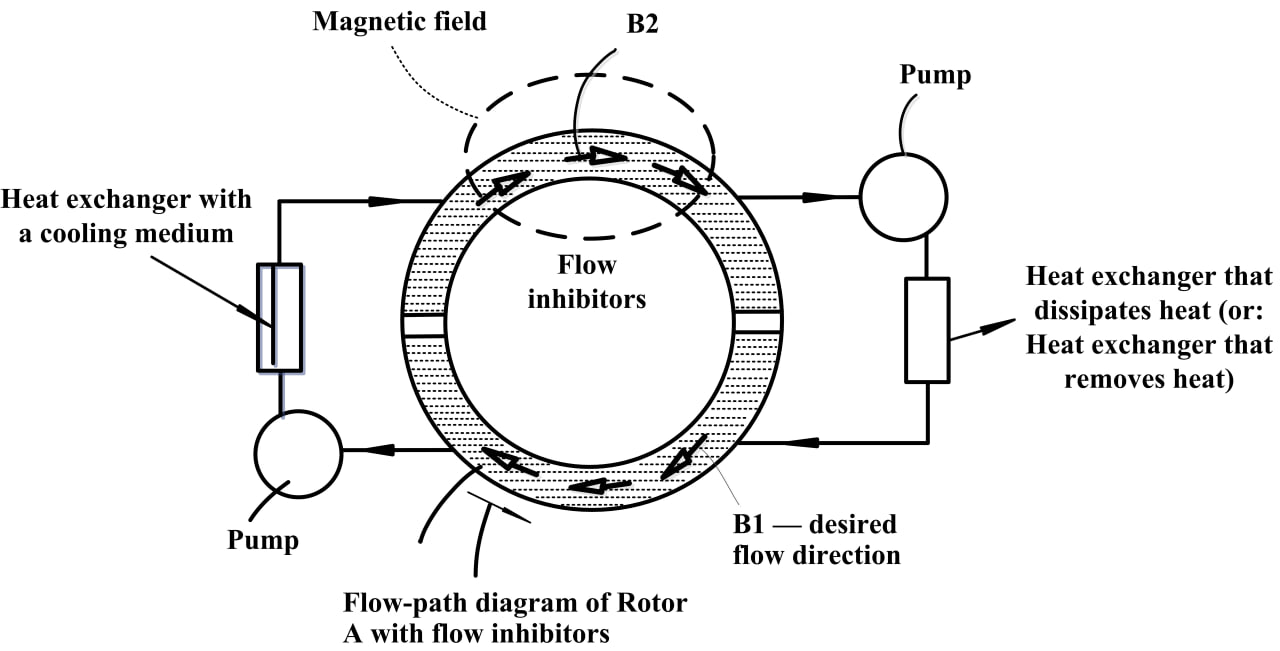
**TABLE 1.** Parameters a, b, and c, unit cell volume V (recalculate) of MnAs1-y Py solid solutions

| *x* | *a,нм* | *b,нм* | *с,нм* | *V*, 10–2 нм3 |
| --- | --- | --- | --- | --- |
| 0,03 | 0,5678 | 0,3627 | 0,6316 | 7,791 |
| 0,05 | 0,5649 | 0,3603 | 0,6285 | 7,749 |
| 0,07 | 0,5631 | 0,3582 | 0,6272 | 7,664 |
| 0,09 | 0,5621 | 0,3567 | 0,6257 | 7,652 |

It was found that with increasing phosphorus concentration, there is a linear decrease in the lattice parameters. The decrease of parameters a, b, and c can be explained by the difference in ionic radii of arsenic and phosphorus [3, 6, 7].

# DISCUSSION

However, partial replacement of Ca by other elements with large ionic radius, such as Wa, Bg, Pb, etc., will increase the Curie temperature and maintain high FEM values. In [4, 7, 10], devoted to the study of magnetic and magnetocaloric properties of magnetic materials, it was shown that the above manganates exhibit significant FEM and their Curie temperatures are near room temperatures. However, the isothermal entropy change was not obtained by the direct method, but from the data of magnetization dependence on temperature and magnetic field using Maxwell's thermodynamic relation. The analysis of numerous experimental data has shown that the data on the values of adiabatic temperature change and isothermal entropy change obtained by the indirect method are not always sufficiently reliable. Often, these data are burdened with a significant error [10, 13]. Thus, the question of measuring the magnetocaloric effect by the direct method at the change of the magnetic field in manganates of different compositions is still topical. The presence of a large number of experimental works on the study of phase transitions and FEM in lanthanum manganates leads to the need to analyze the experimental results with the help of various theoretical models [8, 12]. To date, there are a large number of works in the scientific press that discuss theoretical models that allow describing phase transitions and FEM in various magnetic materials, but theoretical works that allow describing FEM in lanthanum manganates are paragogic absent. The magnetocaloric properties of the studied systems, calculated on the basis of theoretical models, will make it possible to predict new promising composite compositions of manganates, which may be of great practical importance in the future when creating a working body in magnetic cooling devices. One more actual task in magnetic cooling technology is the analysis of heat transfer processes in cells of cooling devices, in which materials with FEM, in particular, manganates, are used as a working body. For the latter materials, theoretical analysis of temperature relaxation times has not been carried out so far, and the ways to increase the efficiency of magnetic materials have not been discussed [7, 14]. The efficiency of magnetic cooling depends not only on the FEM value but also on the value of heat capacity and the magnitude of the change in the magnetic part of entropy under the action of the magnetic field [8]. The value of the lattice part of the entropy Sp, which increases strongly with heating, plays a great role here, due to which magnetic coolers using paramagnetic as working bodies are ineffective at T>20 K. At higher temperatures, magnetically ordered substances are more effective as working bodies, in which large FEMs appear in the region of magnetic phase transitions. In recent years, there is an interest in the creation of new types of magnetic refrigeration machines (MRM) based on the use of FEMs. It is proposed to use rare-earth magnetics, Geisler alloys, manganese arsenide MnAs, compounds Gd5(Si2Ge2), RCo2, La (Fe, Si)13, and others, possessing large FEM and magnetic entropy change in the temperature intervals convenient for operation of such machines, as working bodies [8, 9, 12].



**FIGURE 6.** Schematic diagram of a magnetic refrigeration machine

In one of the MHM designs, a solid working body - a magnetic - cyclically moves between the receiver and the heat source (a cooled body) [13, 15]. In the zone of a strong magnetic field, the working body is isothermally magnetized, and the heat that is released in the working body due to FEM is transferred to the heat receiver. In the zone where there is no magnetic field, the working body is demagnetized, as a result of which the temperature of the working body decreases and heat is transferred to it from the heat source - the cooled body. After equilibrium is established, the cycle is repeated. Thus, the FEM provides the operation of a magnetothermal pump that “pumps” heat from the cooled body [11, 15]. The other promising model of a magnetic refrigeration machine is a device where a liquid with a filler in the form of magnetic particles with a large FEM is pumped through the area in which a strong magnetic field is created.

# CONCLUSION

In the present article, the magnetocaloric properties of MnAs 1 - x P x solid solutions were studied with the focus on the phase composition, structural parameters and the possibilities of using it in magnetic refrigeration. They were determined that lattice parameters linearly decrease with small amounts of phosphorus addition because of the disparity of the ionic radius, and that the samples with a low concentration of phosphorus retain a unique phase structure of orthorhombic (B31). The system will be two phase at greater concentration of phosphorus (y = 0.1). The findings affirm that these materials have the potential of promoting magnetic refrigeration technologies, most particularly when our attention is drawn to their tunability in structure and FEM characteristics near room temperature. Nonetheless, the paper also gives confidence to the weaknesses of the indirect techniques of the FEM measurement and emphasizes the necessity of the direct experimental methods and solid theoretical schemes (especially the ones concerned with the lanthanum manganates and other compounds). Such endeavors are necessary to develop the application of environment friendly and efficient magnetic cooling systems in practice.

# FUTURE SCOPE

# The future studies should aim at advancing the accuracy of FEM measurements through the creation of the direct experimental approaches. The phase transitions and magnetocaloric phenomena in Mn-based materials, especially Mn-based alloys, have to be theoretically modeled, especially within DFT and thermodynamic methods, to predict and optimize the performance.

# Exploring rare-earth substitutions and composite structures can be a solution to improve the FEM and control the Curie temperature. Moreover, an analysis of MnAs-based materials usage in functional prototype cooling systems and their environmental and economical implication will be critical towards commercialization.

# It is also worth putting the emphasis on the development of refrigeration cycles of the next generation, based on active magnetic regeneration and examining smart materials that unite magnetocaloric effects with others, such as magnetoelectric coupling.

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