



ISSN: 0975-833X

RESEARCH ARTICLE

PREPARATION AND CHARACTERIZATION OF Mn_3O_4 NANOPARTICLES BY SOLVO-THERMAL METHOD

¹*Kumar, E., ^{2a}Rajasekaran, S. and ³Muthuraj, D.

¹*Department of Physics, Infant Jesus College of Engineering and Technology, KeelaVallanadu, Thoothukudi, Tamilnadu, India

²Department of Physics, Sri S. Ramasamy Naidu Memorial College, Sattur, Tamilnadu, India

^aPRIST University, Thanjavur, Tamilnadu, India

³Department of Physics, The M.D.T Hindu College, Tirunelveli, Tamilnadu, India

ARTICLE INFO

Article History:

Received 15th December, 2013

Received in revised form

29th January, 2014

Accepted 03rd February, 2014

Published online 25th March, 2014

ABSTRACT

Trimanganesetetroxide (Mn_3O_4) nanoparticles have been synthesized via Microwave Assisted solution method. The structural analysis was carried out using X-ray diffraction. It showed that the Mn_3O_4 nanoparticles exhibited tetragonal hausmannite structure. Grain sizes were estimated from Particle size analyser, XRD and Transmission Electron Microscopy images. The size of the nanoparticles is around 24 nm. The Mn_3O_4 product was investigated by X-ray diffraction, FT-IR, Particle size analyzer, SEM and HRTEM studies.

Key words:

Nanoparticles, Microwave, TEM.

Copyright ©2014 Kumaret al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

INTRODUCTION

Nanomaterials feature high surface energy and reactivity resulting from their high specific surfaces and exhibit special electric, magnetic, absorptive, and catalytic properties (Pan *et al.*, 2007; Huang *et al.*, 2002; Wang and Li 2002; Jain *et al.*, 2005; Tang *et al.*, 2003; Zitoun *et al.*, 2005). Manganese oxides have different forms such as MnO_2 , Mn_2O_3 , Mn_3O_4 , and MnO due to its different oxidation states. Among the above mentioned structures, Mn_3O_4 is one of the stable mixed oxides state ($Mn^{2+}(Mn^{3+})_2O_4$) and having spinel structure. Trimanganesetetroxide is particularly interesting in view of its widespread use in many applications, such as batteries, high-density magnetic storage media, electro-chromic materials and catalysts Shen *et al.*, 1993; Bernardet *et al.*, 1993; Berkowitz *et al.*, 2008; Grootendorst *et al.*, 1995) and also used as an effective catalyst for the decomposition of waste gas and Mn_3O_4 act as a suitable material to control the air pollution (Laugelet *et al.*, 2008). The properties of semiconductor nanostructured materials depend not only on their chemical composition but also on their shape and size. Mn_3O_4 was often synthesized by the high-temperature calcination of either higher manganese oxides (MnO_2 , Mn_5O_8 , and Mn_2O_3), or MnII and MnIII oxysalts, hydroxides, or hydroxyoxides (AlSagheer *et al.*, 1999). In the last decade, various different shape and size

Mn_3O_4 nanocrystals have been synthesized by various techniques, for instance, single-crystal Mn_3O_4 nanorods were obtained by a simple chemical method (Wang *et al.*, 2008); nanoparticles were prepared by oxidation precipitation method (Ozkaya *et al.*, 2008; Chen *et al.*, 2006), vapor phase growth (Chang *et al.*, 2004) and thermal decomposition (Salavati-Niasari *et al.*, 2008; Seo *et al.*, 2004); hierarchical structure with radiated spherulitic nanorods was prepared via a simple solution-based coordinated route, or under mild and organic free template (Wu *et al.*, 2007; Yuan *et al.*, 2005); porous hexagonal plates were prepared by a hydrothermal method (Ren *et al.*, 2008); thin films were prepared by chemical bath deposition (Xu *et al.*, 2006); nano fibers were prepared by sol-gel process (Shao *et al.*, 2004); three dimensional nanostructures were synthesized by soft chemistry templating process (Du *et al.*, 2008). However, the exploration of low-temperature routes for the synthesis of Mn_3O_4 has, therefore, been worth attempting. Recently, nanocrystals like rods were obtained by one-step room-temperature synthesis (Olmos *et al.*, 2005) or by hydrothermal and solvothermal process (Yang, *et al.*, 2006; Zhang *et al.*, 2004), g- Mn_3O_4 nanorods were also gained by one-step low-temperature alcohol-water thermal route (Yang *et al.*, 2004), the uniform and ligand capped nanocrystals with hausmannite structure could be prepared from MnO by controlled chemical oxidation (Yin *et al.*, 2003; Rusakova *et al.*, 2007). Among the various synthesis methods, microwave assisted solution method possess the added

*Corresponding author: Kumar, E.,

Department of Physics, Infant Jesus College of Engineering and Technology, KeelaVallanadu, Thoothukudi, Tamilnadu, India.

advantage of faster reaction time than the conventional solvothermal method. Here, the Mn_3O_4 nanoparticles were prepared at a less reaction time compared to the reaction time of other methods. However, in this study, the Mn_3O_4 nanoparticles were prepared using microwave assisted Solution method. The characteristics such as crystallinity, presence of functional groups, thermogravimetry, and morphology were analyzed using various techniques.

Experimental

Materials

All the chemicals were used as analytical grade without any further purification. Manganese chloride tetra hydrate ($MnCl_2 \cdot 4H_2O$) (AR grade LOBA), Ethylene glycol (EG) (AR grade LOBA) and sodium hydroxide (NaOH) (AR grade MERCK) were used to prepare the nanoparticles of this work. Water used in this investigation was de-ionized water.

Synthesis

Synthesis of Mn_3O_4 nanoparticles

Trimanganesetetroxide (Mn_3O_4) nanoparticles was prepared as follows: the precursors like Manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) and Sodium hydroxide (NaOH) were taken in 1:4 molar ratio and dissolved completely in de-ionized water separately. Then the dissolved $MnCl_2 \cdot 4H_2O$ was added with EG. Further the NaOH solution was added drop wise in to the above mixture under vigorous stirring until the color of the solution was changed in to brown color. Then the prepared mixture solution was kept in the microwave oven (900 W, 2450 MHz., Onida, India) at a temperature of 50 °C for about 30 minutes. Finally, the as prepared sample was centrifuged several times in double distilled water, ethanol and dried at 150 °C for 24hours results in the formation of Mn_3O_4 nanoparticles.

Instrumentation

Powder X-ray diffraction pattern of the nanoparticles was obtained using a powder X-ray diffractometer (PANalytical Model, Nickel filtered Cu K radiations with $\lambda = 1.54056 \text{ \AA}$ at 35 kV, 10 mA). The sample was scanned over the required range for 2θ values (10 – 80°). The FTIR spectrum of the sample was recorded using a Shimadzu 8400S spectrometer by the KBr pellet technique in the range 400-4500 cm^{-1} . The size and shape of nanoparticles was obtained by high resolution transmission electron microscopy (HRTEM) and HRTEM measurements were carried out on a JOEL JEM 2000.

RESULTS AND DISCUSSION

Structural characterization

X-ray diffraction(XRD) studies

The powder XRD pattern for the as-prepared pure Mn_3O_4 nanoparticles is presented in the Figure 1(a). It is observed that the XRD reflection peaks for pure Mn_3O_4 sample are in a perfect match with the diffraction pattern of Mn_3O_4 published in the (JCPDS File No. 24-0734). All the reflections of powder

XRD patterns of this work were indexed using the TREOR and INDEXING software packages. The diffraction peaks of the as prepared Mn_3O_4 samples at $2\theta = 17.98, 28.88, 32.33, 36.1, 38.01, 44.46, 50.71, 58.39, 59.86,$ and 64.73° corresponds to the Miller indices or lattice planes of (101), (112), (103), (211), (004), (220), (105), (321), (224), and (400) respectively. Therefore, it can be indexed to the tetragonal hausmannite structure (space group $I41/amd$) of Mn_3O_4 . The powder XRD pattern of Mn_3O_4 nanoparticles shows broad peaks, which confirmed the formation of small-sized nanoparticles. The particle size of nanoparticles was determined using the Scherrer's relation $d = (0.9 \lambda) / (S \cos \theta)$ where S is the full width at half maximum in radians, λ is the wavelength of X-rays used and θ is the Bragg's angle. For the various reflection peaks of the XRD pattern, the particle size was estimated and the average size of nanoparticles of the sample was found to be around 20 nm. The less intensity of diffracted peaks reveals that the low crystallinity of the as prepared samples. The lattice constants, lattice density, and cell volume of the samples are calculated and are tabulated in Table 1. The obtained lattice constant values are $a=b= 5.769 \text{ \AA}$, $c= 9.46 \text{ \AA}$. These values are in good agreement with the reported values (31-33). The particle size analysis for the sample was carried out using the particle size analyzer (Zetasizer Ver. 6.20 ,Serial Number : MAL1049897). The particle size distribution is presented in the Fig. 2 and it is observed that the size of maximum number of particles is 24.36 nm. It is in good agreement with the particle size observable on the XRD spectrum.

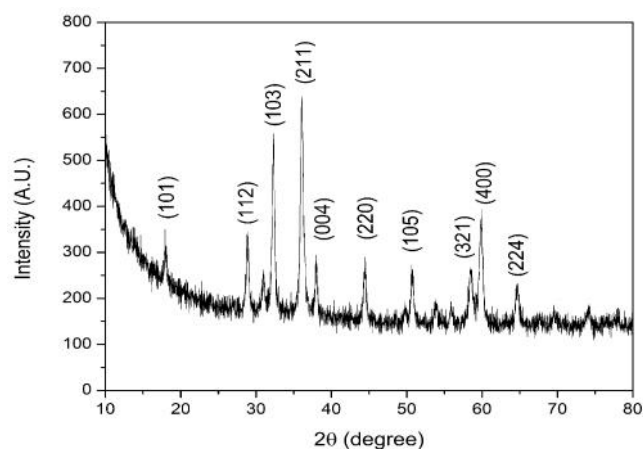


Fig 1. XRD Pattern of as prepared Mn_3O_4 Nanoparticles

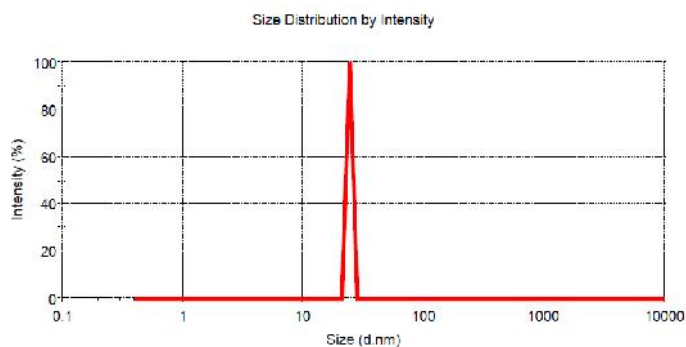


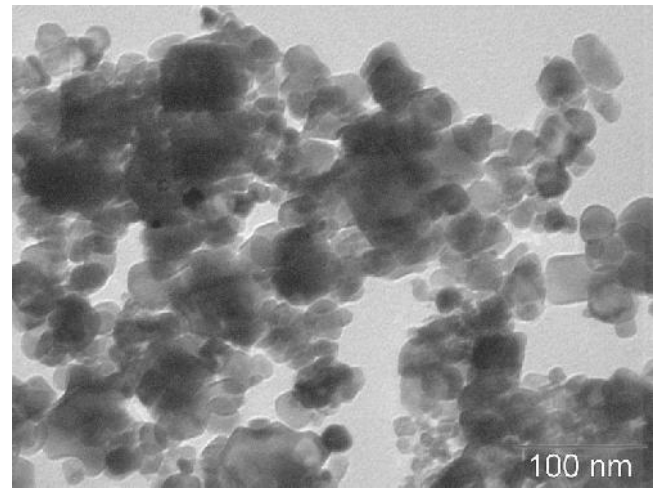
Fig.2. Particle size analyzer spectrum of Mn_3O_4 nanoparticles

Table 1. Structural parameters of Mn₃O₄ samples

Lattice Constant		Grain size in nm	Cell Volume		Lattice density (g/cm ³)
Calculated (Å°)	Standard (Å°)		Calculated (Å°)	Standard (Å°)	
a=b= 5.7699	a=b= 5.763	24	315.159	314.05	4.822
c= 9.466714	c= 9.456				

Transmission Electron Microscopic (TEM) studies of Mn₃O₄ nanoparticles

The information such as particle size, size distribution, shape, degree of agglomeration etc of Mn₃O₄ nanoparticles are obtained from Transmission Electron Microscopy (TEM). The TEM overview images were presented in Figs. 3, from the image it is concluded that the nanoparticles are of uniform in size and shape. It is observed that the shapes of most of the particles are nearly spherical and slightly elongated. The selected area electron diffraction (SAED) pattern of nanoparticle is shown in the Fig. 4. The high crystallinity of the powder leads to its corresponding well-pronounced Debye-Scherrer diffraction rings in the SAED pattern that can be assigned to the reflections (101), (112), (103), (211), (004), (220), (105), and (400) of tetragonal hausmannite structure of Mn₃O₄. There are no additional rings in the SAED pattern stemming from any crystalline impurities. To get further insight into the atomic order of the Mn₃O₄ nanoparticles, high-resolution images were recorded. To obtain a particle size distribution from transmission electron micrographs we manually measured the particle sizes for 50 particles to ensure a reliable representation of the actual size distribution. The crystallite size is about 20-40 nm as estimated from the TEM micrographs. The experimental and calculated XRD patterns provide a volume-weighted average grain size of 24 nm, which is in good agreement with the particle size observable on the TEM image.

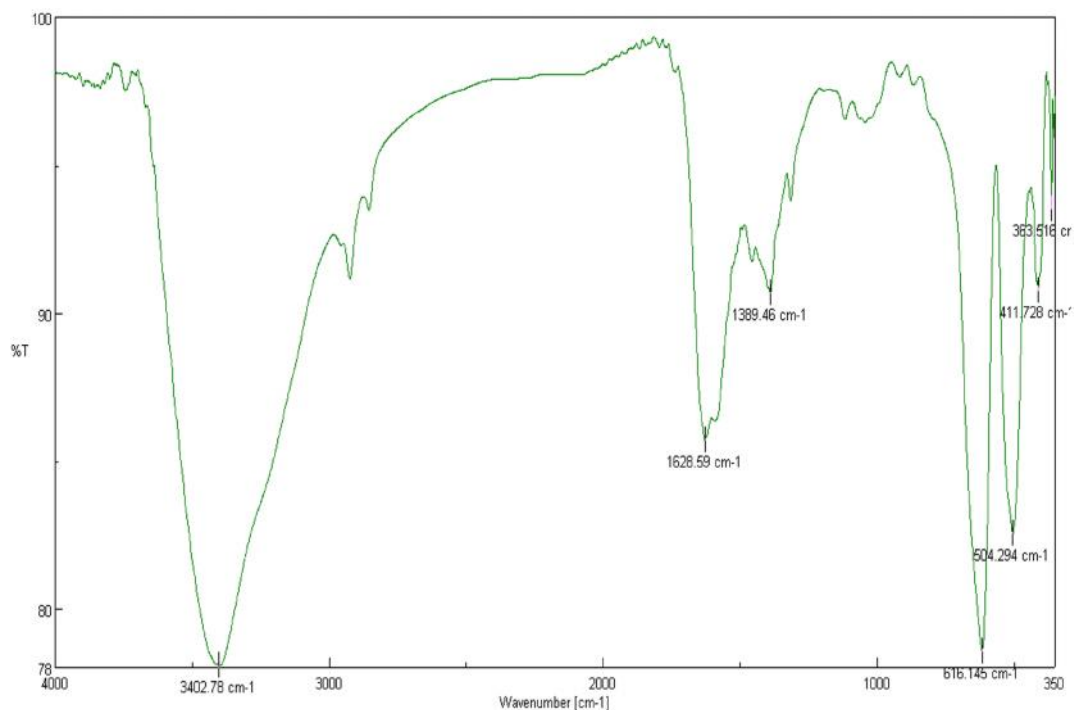
**Fig. 3. TEM image of the Mn₃O₄ nanoparticles**

FT-IR Analysis

The presence of functional groups in Mn₃O₄ samples are identified through FT-IR analysis. Figure 5 shows the FT-IR spectra of Mn₃O₄ samples. The observed different modes and its corresponding wave numbers are given in Table 2.

Table 2. Assignments of FTIR spectra of the samples

Wavenumbers(cm ⁻¹)	Modes of vibration
3402.78	-OH group
1628.46	Adsorption of water moisture
1389.59	Bending vibration of O-H bonds connected with Mn atoms
616.14	Mn-O stretching mode in tetrahedral sites
504.29	Distortion vibration of Mn-O in an octahedral site
414.72	

**Fig. 3.4 FTIR spectra of the Mn₃O₄ nanoparticles**

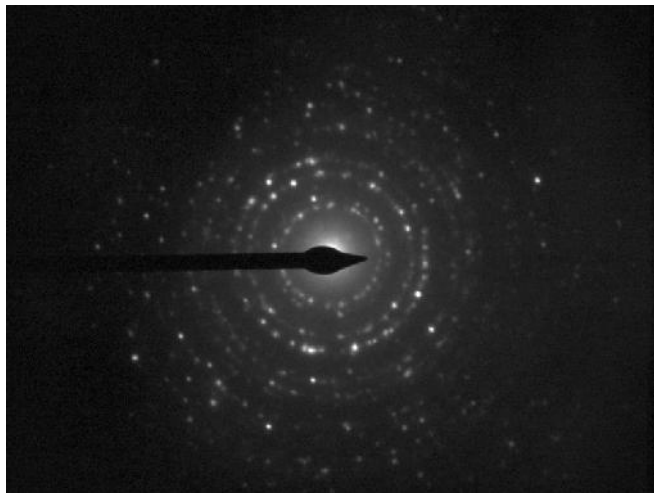


Fig. 4. SAED pattern of the Mn₃O₄ nanoparticles

The samples show a broad band around 3402 cm⁻¹ indicating the presence of -OH group in the as prepared samples. The small bands are observed at approximately 1628 cm⁻¹ and 1389 cm⁻¹ corresponds to the adsorption of molecules from moisture and bending vibration of O-H joined with metal (Mn) atoms. The two significant peaks observed at approximately 614, 504 and 414 cm⁻¹ that reveals the coupling between the Mn-O stretching modes of tetrahedral and octahedral sites respectively. That is, the vibration band around 614 cm⁻¹ corresponds to the characteristics of Mn-O stretching mode in tetrahedral sites, similarly the vibration band observed around 504 and 414 cm⁻¹ is associated with distortion vibration of Mn-O in an octahedral site (Dubal et al., 2010; Dubal et al., 2010; Xing et al., 2011; Baykal et al., 2010).

Conclusion

In summary, Mn₃O₄ nanoparticles were prepared by microwave assisted solution method. The phase formation, purity of sample, particle size and the presence of functional groups are identified through XRD, FTIR, Particle size analyser and TEM analysis. Mn₃O₄ nanoparticles exhibit a crystallite size around 24 nm. It is confirmed by XRD, Particle size analyser and TEM studies.

REFERENCES

AlSagheer F.A., M.A. Hasan, L. Pasupulety, M.I. Zaki, *J. Mater. Sci. Lett.* 18 1999.209–211.
 Baykal A., H. Kavas, Z. Durmu, M. Demir, S. Kazan, R. Topkaya, M.S. Toprak, *Central European Journal of Chemistry*, 8(3) 2010 633-638.
 Berkowitz AE, Rodriguez GF, Hong JI, An K, Hyeon T, Agarwal N, et al. *Phys Rev B*, 2008;77:024403.
 Bernard MC, Goff HL, Thi BV. *J Electrochem Soc* 1993; 140:3065–70.
 Chang Y.Q., X.Y. Xu, X.H. Luo, C.P. Chen, D.P. Yu, *J. Cryst. Growth* 264, 2004.232–236.
 Chen Z.W., J.K.L. Lai, C.H. Shek, *Scripta Materialia* 55 2006.735–738.
 Du C., J. Yun, R.K. Dumas, X. Yuan, K. Liu, N.D. Browning, N. Pan, *Acta Materialia* 56, 2008, 3516–3522.

Dubal D.P., D.S. Dhawale, R.R. Salunkhe, S.M. Pawar, C.D. Lokhande, *Appl Surf Sci*, 256, 2010. 4411–4416.
 Dubal D.P., D.S. Dhawale, R.R. Salunkhe, V.J. Fulari, C.D. Lokhande, *J Alloys Compd*, 497, 2010. 166 – 170.
 Grootendorst EJ, Verbeek Y, Ponce V. *J Catal* 1995;157:706–12.
 Huang H., S.C. Yin, T. Kerr, N. Taylor, L.F. Nazar, *Adv. Mater.* 14, 2002. 1525–1528.
 Jain G., J. Yang, M. Balasubramanian, J.J. Xu, *Chem. Mater.* 17, 2005. 3850–3860.
 Laugel G., J. Arichi, H. Guerba, M. Molie`re, A. Kiennemann, F. Garin, B. Louis, *Catal Lett*, 125, 2008.14–21.
 Li Y., H. Tan, X.Y. Yang, B. Goris, J. Verbeeck, S. Bals, P. Colson, R. Cloots, G.V. Tendeloo, B.L. Su, *Small*, 4, 2011.475–483.
 Olmos A.V., R. Redon, G.R. Gattorno, M.E.M. Zamora, F.M. Leal, A.L.F. Osorio, J.M. Saniger, *J. Colloid Sci.* 291 2005.175–180.
 Ozkaya, T., A. Baykal, H. Kavas, Y. Koseoglu, M.S. Toprak, *J. Physica B* 403, 2008.3760–3764.
 Pan J.Q., Y.Z. Sun, Z.H. Wang, P.Y. Wan, X.G. Liu, M.H. Fan, *J. Mater. Chem.* 17, 2007. 4820–4825.
 Ren T., Z.Y. Yuan, W. Hu, X. Zou, *Micropor. Mesopor. Mater.* 112 2008.467–473.
 Rusakova I., T. Ould-Ely, C. Hofmann, D. Prieto-Centurion, C.S. Levin, N.J. Halas, A. Luetzge, K.H. Whitmire, *Chem. Mater.* 19, 2007.1369–1375.
 Salavati-Niasari M., F. Davar, M. Mazaheri, *Polyhedron* 27, 2008.3467–3471.
 Seo W.S., H.H. Jo, K. Lee, B. Kim, S.J. Oh, J.T. Park, *Angew. Chem. Int. Ed. Engl.* 43, 2004 1115–1117.
 Shao C., H. Guan, Y. Liu, X. Li, X. Yang, *J. Solid State Chem.* 177, 2004. 2628–2631.
 Shen YF, Zenger RP, Deguzman RN, Suib SI, Mccurdy L, Potter DI, et al. *Science*, 1993;260: 511260: 511.
 Tang W.P., X.J. Yang, Z.H. Liu, K. Ooi, *J. Mater. Chem.* 13, 2003.2989–2995.
 Wang X., Y. Li, *J. Am. Chem. Soc.* 124 2002. 2880–2881.
 Wang Z.H., D.Y. Geng, Y.J. Zhang, Z.D. Zhang, *J. Cryst. Growth* 310, 2008. 4148–4151.
 Wu Z., K. Yu, Y. Huang, C. Pan, Y. Xie, *J. Chem. Cent.* 1, 2007.1–9.
 Xing S., Z. Zhou, Z. Ma, Y. Wu, *Mater Lett*, 65, 2011.517–519.
 Xu, H. Y. S. L. Xu, X. D. Li, H. Wang, H. Yan, *J. Appl. Surf. Sci.* 252, 2006. 4091–4096.
 Yang B., H. Hu, C. Li, X. Yang, Q. Li, Y. Qian, *Chem. Lett.* 33, 2004.804–805.
 Yang Z., Y. Zhang, W. Zhang, X. Wang, Y. Qian, X. Wen, S. Yang, *J. Solid State Chem.* 179, 2006. 679–684.
 Yin M., S. O'Brien, *J. Am. Chem. Soc.* 125, 2003.10180–10181.
 Yuan J., W. N. Li, S. Gomez, S. L. Suib, *J. Am. Chem. Soc.* 127, 2005.14184–14185.
 Zhang F., X. G. Zhang, L. Hao, *Mater Chem Phys*, 126, 2011.853–858.
 Zhang Y. C., T. Qiao, X. Y. Hu, *J. Solid State Chem.* 177, 2004. 4093–4097.
 Zitoun D., N. Pinna, N. Frolet, C. Belin, *J. Am. Chem. Soc.* 127, 2005. 15034–15035.
