Synthesis and characterization of BaNiO₃ using a solid-state thermal decomposition method and the preparation of its stable aqueous suspension

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Abstract. In the present study, the preparation of BaNiO₃ nano-oxide is reported via simple solid-state thermal decomposition of [Ba(en)₄][Ni(H₂O)₂(NCS)₄] precursor complex for the first time. As-prepared nano-oxide was coated by citric acid to form a stable aqueous magnetic suspension. The precursor complex was characterized by conductivity measurements, ultra violet–visible spectroscopy, elemental analysis and Fourier transform infrared spectroscopy. The composition of the perovskite was confirmed by energy-dispersive X-ray spectroscopy analysis and the hexagonal structure was supported by powder X-ray diffraction. In addition, monotonous morphology of the nano-oxide was illustrated by field-emission scanning electron microscopy. Superparamagnetism of the nanoparticles were detected using a vibrating sample magnetometer. Finally, the hydrodynamic size as well as the zeta potential of the pristine and surface-treated BaNiO₃ nano-oxide were measured in deionized water via a dynamic light scattering analyzer and they were compared. Results show the excellent stability of the surface-modified magnetic oxide compared to the pristine.

Keywords. Oxides; perovskite; magnetic fluid; XRD; SEM; VSM.

1. Introduction

Magnetic nano-oxides have attracted wide attention due to their dimensions and magnetism, which give a miracle efficiency to these tiny particles and enhance their features against their bulks. Since the first investigation, magnetic nanoparticles have been applied in a vast range of properties such as ceramics, electronic materials [1], heterogeneous catalysis [2], different types of sensors [3], contrast agents for magnetic resonance imaging (MRI) [4], cancer therapy [5], magnetic labels for biosensing [6] and various magnetic compounds [7]. Among the oxides, perovskites are of a special interest. Compounds expressed as ABX₃, where A is a large cation, B is a small cation and X is an anion, are known as perovskites [8]. Since the development of perovskites, they have been patented and applied in different facets of industry owing to their low price, adaptability and thermal stability. These oxides have also been highly explored for their catalytic, electrical, magnetic and optical properties. They have been even studied for environmental catalytic applications [9]. The structure of barium nickel perovskite was studied through X-ray diffraction (XRD) and single crystal analysis for the first time [10,11] and its magnetic properties were pointed out by Takeda *et al* [12] in 1974. According to earlier studies, BaNiO₃ has a close-packed hexagonal structure, which is stabilized by large cations [13]. Nickel–barium perovskites are known to

have several advantages, such as excellent magnetic properties, chemical and corrosion resistances as well as strong hardness [14–17]. Despite these advantages (to the best of our knowledge), there was no work on nanosized-BaNiO₃, since the development of BaNiO₃ in 1974.

There are a number of chemical solution-based as well as solid-state methods for preparation of magnetic nano-oxides (including perovskites) such as wet inoculation [18], co-precipitation [19], aerosol [20,21], solution–gel [22], wet thermal decomposition [23] and dry thermal decomposition of precursor complex [24,26]. Solid-state thermal decomposition of precursor complex is a chemical decomposition which is created by heat. In the process, the appropriate temperature produces an explosion and decomposes the precursor complex provided that the reaction is exothermic [27–31]. This method is known as a cost-effective, simple and environmentally friendly strategy for synthesis of nano-oxides.

For industrial and medicinal applications, magnetic nano-oxides are usually dispersed in organic or aqueous solvents [32]. However, the particles' tendencies to aggregate in solutions, especially when the size of nanoparticles is in the range of superparamagnetism (<20 nm), prevent the preparation of stable suspension. To overcome this obstacle, magnetic nanoparticles are usually coated with organic or inorganic materials, which eventually results in the formation of magnetic fluids. Magnetic fluids were designed for the first time

in the 1960s by Stephen Papell [33]. In water-based magnetic fluids, the magnetic particles might have various coating molecules, which make them stable in aqueous liquids [34–37]. Among the molecules, $C_6H_8O_7$ (citric acid) has been largely applied for the synthesis of aqueous stable nanoparticles [38–45]. Citric acid has the capability of being adsorbed onto the surface of the oxide by coordinating via one or two

Figure 1. Structural illustration of the cationic part of the prepared precursor complex.

Figure 2. Structural illustration of the anionic part of the prepared precursor complex.

of its carboxylate groups. It prevents particle agglomeration and provides a hydrophilic surface for the oxide, by leaving at least one of its carboxylic acid groups dangled [46].

In this investigation, $BaNiO_3$ nanoperovskite was prepared by solid-state thermal decomposition of $[Ba(en)_4][Ni(H_2O)_2(NCS)_4]$ novel precursor complex and then, the prepared nano-oxide was surface-modified by citric acid to form a stable, superparamagnetic aqueous fluid.

2. Experimental

2.1 Materials

Barium chloride ($BaCl_2 \cdot 2H_2O$, +99%, Merck), nickel chloride ($NiCl_2$, +99%, Merck), ammonium thiocyanate (NH_4SCN , +99%, Merck), ethylenediamine (98%, Aldrich), citric acid ($C_6H_8O_7$, +99%, Sigma-Aldrich) and ethanol (99.5%, Aldrich) were utilized as raw materials without further purification.

2.1a Preparation of precursor complex: Each of the two ionic parts of the precursor complex was prepared in separate Florence flask and in the final step, they were mixed. For preparation of the cation (figure 1), 1 mmol of $BaCl_2 \cdot 2H_2O$ was added to distilled water (15 ml) and stirred vigorously. To this, a solution of ethylenediamine (4 mmol) in ethanol (15 ml) was added followed by stirring (80°C, 12 h).

The anionic part of the precursor complex (figure 2) was prepared in a Florence flask. One mmol of $NiCl_2$ was

Figure 3. Representation of FT-IR spectrum for the prepared precursor complex at room temperature.

dissolved in distilled water (10 ml) followed by the addition of a NH₄SCN (4 mmol) solution in distilled water (5 ml).

Figure 4. Representation of absorption spectra for the precursor complex aqueous solutions at room temperature: (a) 10^{-5} M and (b) 10^{-3} M.

Figure 5. TGA curve of the precursor complex in air.

The mixture was refluxed at 80°C and remained at that temperature for 12 h till the reaction is completed. On the next stage, the crystals were obtained by mixing the cationic and anionic parts of the precursor complex, followed by filtration and then exposure to the air. Anal. Calc. for C₁₂H₃₆BaNi₁₂NiO₂S₄: C, 20.45; H, 5.15; N, 23.85; O, 4.54; S, 18.19. Found: C, 19.36; H, 4.11; N, 22.73; O, 7.01; S, 17.09% (68% yield).

2.1b Preparation of nano-oxide and coating procedure:

The pure crystals of the precursor complex were placed in a crucible and heated to 850°C (5°C min⁻¹). The crystals were remained at that temperature for 2 h in normal atmosphere to form the perovskite nanoparticles.

The coating process was similar to those of previously applied, as the two step method for the preparation of citric acid-coated iron oxide nanoparticles (see details in ref. [47]). In summary, the synthesized oxide was dispersed in deionized water under sonication. The suspension was heated to 90°C, followed by the addition of citric acid and the heating procedure continued for 1 h under vigorous stirring. The product was finally washed with deionized water.

2.2 Methods of characterization

Fourier transform infrared (FT-IR) spectra were recorded by JASCO 460PLUS FT-IR (10:1 KBr per sample). Ultra violet-visible spectroscopy (UV-Vis) measurements were performed on a JASCO5870 UV-Vis spectrometer. The molar conductivity measurement was recorded at room temperature using a Ciba Corning model check-mate 90 conductometer. Composition of the prepared precursor complex was revealed through the measurements of C, H, O, S and N using a Pekin-Elmer 2400 CHNS/O elemental analyzer. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50H (20 ml min⁻¹, 10°C min⁻¹). The X-ray pattern was obtained in 2θ range of 0–90° radiation via Philips X'Pert MPD (40 KV Co

Figure 6. XRD pattern of the pristine BaNiO₃ nanoparticles at room temperature.

Figure 7. FE-SEM image for the pristine nano-oxide.

Table 1. EDS results for the pristine BaNiO₃.

Element	A%	W%
O	56.96	17.91
Ni	23.15	26.48
Ba	18.36	49.79
Au	1.53	5.92

anode X-ray tube, 1.78897 Å). In addition, the field-emission scanning electron microscopy (FE-SEM) image was taken on FE-SEM Hitachi, S4800 equipped with energy-dispersive X-ray spectroscopy (EDS) using gold-coated samples. A vibrating sample magnetometer (Lake Shore 7400) recorded the magnetic features of the prepared nano-oxide. And finally, size distribution as well as zeta potential analysis were

performed at 90° angle and 20°C via a Malvern Zetasizer 3000HSA UK equipped with a He–Ne laser (10 mW, 633 nm).

3. Results and discussion

3.1 Characterization of the prepared ionic precursor complex

Figure 3 illustrates the FT-IR spectrum of [Ba(en)₄][Ni(H₂O)₂(NCS)₄]. The absorption bands in the figure confirm both the presence and convenient coordination of the ligands in the compound. The peak at 2052 cm⁻¹ is referred to stretching vibration of C≡N in isothiocyanate. Absorption bands at 487 and 600 cm⁻¹ belong to Ni–N and Ba–N stretching vibrations, respectively. Also, 1200, 1600 and 3583 cm⁻¹ are detected for bending, symmetric and asymmetric stretching vibrations of OH in the coordinated water, respectively [48–51].

The two electron absorption bands at 214 and 273 nm in the absorption spectrum (figure 4a) can be assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ (intra-ligand) electron transfers in thiocyanate, respectively. In addition, the absorption bands at 393, 657 and 720 nm in figure 4b represent the d → d electron transfers of the metal (Ni(II)). According to literature, no absorption is expected for Ba(II) in the prepared precursor complex [52].

The conductivity measurements for [Ba(en)₄][Ni(H₂O)₂(NCS)₄] in distillate water (2×10^{-4} M) revealed that the synthesized precursor complex is a two-ion electrolyte with the conductance of 126.6 cm² Ω⁻¹ mol⁻¹. This is in agreement with the literature (where 100–131 cm² Ω⁻¹ mol⁻¹ is expected for the conductivity of two ion structures in solution) [53].

As shown in figure 5, thermal decomposition of [Ba(en)₄][Ni(H₂O)₂(NCS)₄] takes place in three steps. It is suggested that in the first step, at 100–215°C, the precursor complex

Figure 8. EDS pattern for the pristine BaNiO₃.

loses the coordinated water molecules and carbons in coordinated ligands. In the next step (520–610°C), the precursor complex is decomposed to nitride and sulfide salts and finally, the solid-state decomposition takes place in the range of 600–790°C. Therefore, 850°C was selected as the appropriate calcination temperature for the precursor complex.

3.2 Characterization of the pristine and coated nano-oxide

Figure 6 represents the X-ray pattern for the prepared ultra-fine BaNiO₃ perovskite (JCPDS no. 01-072-0404, hexagonal, $P63mc$, $a = 5.6310$, $b = 5.6310$ and $c = 4.8080$ Å, max. diff. $2\theta = 30.29^\circ$, $hkl = 101$, $d = 3.42$ Å). The

Figure 9. VSM graph for the pristine BaNiO₃ at room temperature.

crystallite size of the particles was calculated as 4.90 nm by Debye–Scherrer equation (Eq. 1) [54].

$$D_c = K\lambda/\beta \cos \theta. \quad (1)$$

Along the above measurements, figure 7 illustrates FE-SEM image of the gold-coated nanoparticles, in which uniform morphology and spherical shape of the crystals can be easily observed. EDS analysis also confirmed the projected composition for the prepared perovskite. The results can be seen in table 1 and figure 8.

Figure 9 represents the hysteresis loop for the synthesized nano-oxide measured by vibrating sample magnetometer (VSM). No remanent magnetization as well as coercivity is detected for the nano-oxide. The saturation magnetization is also reported as 22.9 emu g⁻¹. Results indicate the superparamagnetic behaviour of BaNiO₃ in room temperature. This phenomenon can be stemmed from the particle size and the presence of magnetic single domains [55].

FT-IR spectrum for citric acid-coated BaNiO₃ nanocrystals (figure 10) shows a strong absorption band at 3447 cm⁻¹ belongs to asymmetric stretching vibration of OH groups in citric acid. The peak at 1609 cm⁻¹ is assigned to symmetric stretching vibration of C=O in COOH and the absorption band at 1412 is referred to the asymmetric stretching vibration of C–O in COO⁻. The absorption bands at 400–600 can be assigned to metal-oxygen vibrations (491 for Ba–O and 593 cm⁻¹ for Ni–O).

After the characterization procedure, the hydrodynamic size as well as the zeta potential of the pristine and coated particles were compared in deionized water.

As observed from table 2, the hydrodynamic size of the coated oxide in deionized water (24.1 nm) is slightly

Figure 10. FT-IR spectrum of the citric acid-coated BaNiO₃ at room temperature.

Table 2. Values determined by dynamic light scattering analysis in deionized water for both the pristine and the surface-treated BaNiO₃ nanoparticles at 20°C and pH = 7.

NPs	Hydrodynamic size (nm)	Zeta potential (mV)
Pristine	18.3	+15.3
Coated	24.1	−49.9

different from the hydrodynamic size of the pristine oxide. In other words, surface modification of the nanoparticles by citric acid has not significantly affected the particle size. However, there is a large difference between the two values of zeta potentials for the pristine as well as the surface-treated oxide. Generally, colloidal particles were found to be stable if their zeta potentials (for both negative and positive zeta potentials) surpass a certain value and are observed to aggregate at lower values [56]. The proposed explanation for this difference is that the presence of negatively charged carboxylic groups on the surface of citric acid-coated particles, which change the positive zeta potential and make the nano-oxide hydrophilic.

4. Conclusions

According to the results, the nanoparticles of BaNiO₃ were successfully prepared using solid-state thermal decomposition of [Ba(en)₄][Ni(H₂O)₂(NCS)₄], and then the unstable aqueous suspension of BaNiO₃ was turned to a stable aqueous suspension by surface treating of the pristine oxide using citric acid. The simplicity of preparation and the unique features of the prepared magnetic oxide may establish a new generation of cost-effective magnetic fluids.

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References

- [1] Becker P 1998 *Adv. Mater.* **10** 979
- [2] Enache D I, Rebours B, Auberger M R and Revel R 2002 *J. Catal.* **205** 346
- [3] Laureiro Y, Camps M D, Veiga M L, Jerez A and Pico C 1988 *Eur. J. Solid State Inorg. Chem.* **25** 381
- [4] Wagner S 2002 *Investig. Radiol.* **37** 167
- [5] Hilger I, Frühauf K, Andrä W, Hiergeist R, Hergt R and Kaiser W A 2002 *Acad. Radiol.* **9** 198
- [6] Li G, Sun S, Wilson R J, White R L, Pourmand N and Wang S X 2006 *Sens. Actuators A: Phys.* **126** 98
- [7] Whitaker A and Channell A D 1993 *J. Mater. Sci.* **28** 2489
- [8] Katz L and Ward R 1964 *Inorg. Chem.* **3** 205
- [9] Labhasetwar N, Saravanan G, Megarajan S K, Manwar N, Khobragade R, Doggali P et al 2015 *Sci. Tech. Adv. Mater.* **16** 1
- [10] Lander J 1951 *Acta Crystallogr.* **4** 148
- [11] Takeda Y, Kanamaru F, Shimada M and Koizumi M 1976 *Acta Crystallogr.* **32** 2464
- [12] Takeda Y, Shimada M, Kanamaru F, Koizumi M and Yamamoto N 1974 *Chem. Lett.* **2** 107
- [13] Longo J M and Kafalas J A 1968 *Mater. Res. Bull.* **3** 687
- [14] Goldman A 2006 *Modern ferrite technology*, 2nd edn (New York: Springer) p 403
- [15] Benito G, Morales M P, Requena J, Raposo V, Vazquez M and Moya J S 2001 *J. Magn. Magn. Mater.* **234** 65
- [16] Cullity B D 1972 *Introduction to magnetic materials*, 1st edn (USA: Addison-Wesley Co.) p 89
- [17] O'Handley R C 2000 *Modern magnetic materials: principles and applications* 2nd edn (USA: Wiley-Interscience Publications) p 469
- [18] Shi T, Li H, Yao L, Ji W and Au C T 2012 *Appl. Catal. A-Gen.* **425** 68
- [19] Mirzaei A A, Shirzadi B, Atashi H and Mansouri M 2012 *J. Ind. Eng. Chem.* **18** 1515
- [20] Gonzalez-Carreno T, Morales M P and Serna C J 2000 *Mater. Lett.* **43** 97
- [21] Lopez-Navarrete E, Gonzalez-Elipe A R and Ocana M 2003 *Ceram. Int.* **29** 385
- [22] Gajendran P and Saraswathi R 2007 *J. Phys. Chem.* **111** 11320
- [23] Park J, An K, Hwang Y, Park J G, Noh H J, Kim J Y et al 2004 *Nature Mater.* **3** 891
- [24] Saravani H, Esmaeilzadei M R and Ghahfarokhi M T 2016 *J. Inorg. Organomet. P.* **26** 353
- [25] Salavati-Niasari M, Mohandes F, Davar F, Mazaheri M, Monemzadeh M and Yavarinia N 2009 *Inorganica Chim. Acta* **362** 3691
- [26] Saravani H, Ghahfarokhi M T and Esmaeilzadei M R 2016 *J. Inorg. Organomet. Polym. Mater.* **26** 660
- [27] Turcotte R, Vachon M, Kwok Q S M, Wang R and Jones D E G 2005 *Thermochim. Acta* **433** 105
- [28] Salavati-Niasari M, Mir N and Davar F 2009 *J. Phys. Chem. Solids* **70** 847
- [29] Striebig R C and Lawrence J 2003 *J. Anal. Appl. Pyrol.* **70** 339
- [30] Hosseinpour-Mashkani S M and Ramezani M 2014 *Mater. Lett.* **130** 259
- [31] Sobhani M, Salavati-Niasari and Hosseinpour-Mashkani S M 2012 *J. Clust. Sci.* **23** 1143
- [32] Saiyed Z M, Telang S D and Ramchand C N 2004 *Indian J. Eng. Mater. Sci.* **11** 358
- [33] Papell S S 1965 U.S. Patent no. 3, **215** 572
- [34] Radbruch A, Mechtold B, Thiel A, Miltenyi S and Püger E 1994 *Methods Cell Biol.* **42** 387
- [35] Pouliquen D, Perroud H, Calza F, Jallet P and Le Jeune J J 1992 *Magn. Reson. Med.* **24** 75
- [36] Jordan A, Wust P, Fähling H, John W, Hinz A and Felix R 1993 *Int. J. Hypertherm.* **9** 51
- [37] Läubbe A S, Alexiou C and Bergemann C 2001 *J. Surg. Res.* **95** 200
- [38] Nigam S, Barick K and Bahadur D 2011 *J. Magn. Magn. Mater.* **323** 237
- [39] Boyer C, Whittaker M R, Bulmus V, Liu J and Davis T P 2010 *NPG Asia Mater.* **2** 23

- [40] Munnier E, Cohen-Jonathan S, Linassier C, Douziech-Eyrolles L, Marchais H, Soucé M *et al* 2008 *Int. J. Pharmaceut.* **363** 170
- [41] Wani K D, Kitture R, Ahmed A, Choudhari A S, Koppikar S J, Kale S N *et al* 2011 *J. Bionanosci.* **5** 59
- [42] Daniele M A, Shaughnessy M L, Roeder R, Childress A, Bandera Y P and Foulger S 2012 *ACS Nano* **7** 203
- [43] Fortin J P, Gazeau F and Wilhelm C 2008 *Eur. Biophys. J.* **37** 223
- [44] Li L, Mak K, Leung C, Chan K, Chan W, Zhong W *et al* 2012 *IEEE Trans. Magn.* **48** 3299
- [45] Lapresta-Fernández A, Doussineau T, Dutz S, Steiniger F, Moro A J and Mohr G J 2011 *Nanotechnology* **22** 415501
- [46] Liu C and Huang P 1999 *Soil Sci. Soc. Am. J.* **63** 65
- [47] Li L, Mak K Y, Leung C W, Chan K Y, Chan W K, Zhong W *et al* 2013 *Microelectron. Eng.* **110** 329
- [48] Nakamoto K 2008 *Infrared and Raman spectra of inorganic and coordination compounds*, Part B, 6th edn (New York: Wiley) p 1
- [49] Chattopadhyay S K, Hussain M, Ghosh S and Guha A K 1990 *Trans. Metal. Chem.* **15** 473
- [50] Chattopadhyay S K and Ghosh S 1987 *Inorg. Chim. Acta* **131** 15
- [51] Chattopadhyay S K and Ghosh S 1989 *Inorg. Chim. Acta* **163** 245
- [52] Lever A B P 1984 *Inorganic electronic spectroscopy* 2nd edn (Amsterdam: Elsevier) p 507
- [53] Devereux M, McCann M, Leon V, McKee V and Ball R J 2002 *Polyhedron* **21** 1063
- [54] Hosseinpour-Mashkani S M, Mohandes F, Salavati-Niasari M and Venkateswara-Rao K 2012 *Mater. Res. Bull.* **47** 3148
- [55] Jiang W, Liu Y, Li F, Chu J and Chen K 2010 *Mater. Sci. Eng. B-Adv.* **166** 132
- [56] Elimelech M, Jia X, Gregory J and Williams 1995 *Particle deposition and aggregation: measurement, modelling and simulation* (USA: Butterworth-Heinemann) p 24