ภาคผนวก

ไฟล์มาตรฐาน JCPDS หมายเลข 00-024-0033 (Hydroxyapatite)

ไฟล์มาตรฐาน JCPDS หมายเลข 00-002-1216 (Nickel oxide)

งานวิจัยที่ได้รับการเผยแพร่

Name and formula

Reference code:	00-024-0033

Mineral name:	Hydroxylapatite
PDF index name:	Calcium Phosphate Hydroxide

Empirical formula:	$Ca_5HO_{13}P_3$
Chemical formula:	$Ca_5 (PO_4)_3 (OH)$

Crystallographic parameters

Crystal system:	Hexagonal
Space group:	P63/m
Space group number:	176

a (?):	9.4320
b (?):	9.4320
c (?):	6.8810
Alpha (?):	90.0000
Beta (?):	90.0000
Gamma (?):	120.0000

Calculated density (g/cm^3):	3.14
Volume of cell (10^6 pm^3):	530.14
Z:	2.00

RIR:	-

Status, subfiles and quality

Status:	Marked as deleted by ICDD
Subfiles:	Inorganic Mineral Pharmaceutical
Quality:	Calculated (C)

Comments

Deleted by:	Deleted by mineral 1980.

References

Primary reference:	Smith et al., *ICDD Grant-in-Aid*, (1973)
Additional pattern:	Posner et al., *Acta Crystallogr.*, **11**, 308, (1958)

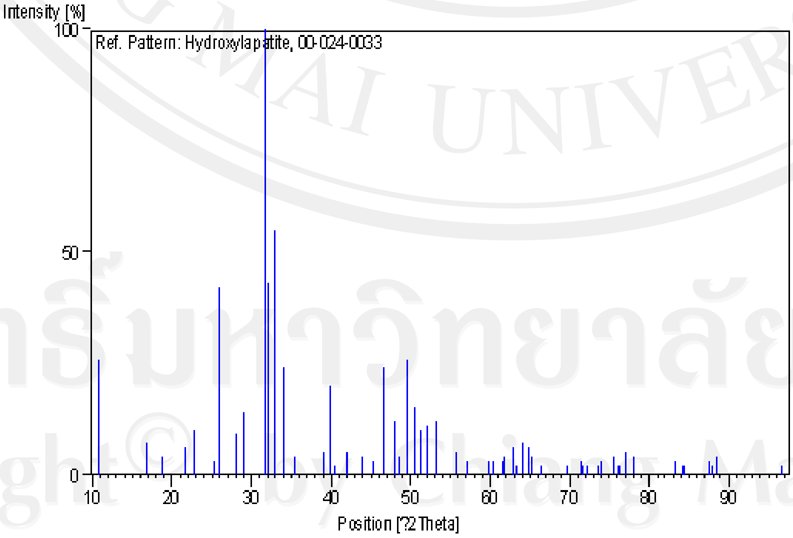
Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	0	0	8.16800	10.823	26.0
2	1	0	1	5.26300	16.832	7.0
3	1	1	0	4.71600	18.801	4.0
4	2	0	0	4.08400	21.743	6.0
5	1	1	1	3.89000	22.842	10.0
6	2	0	1	3.51200	25.339	3.0
7	0	0	2	3.44000	25.879	42.0
8	1	0	2	3.17100	28.117	9.0
9	2	1	0	3.08700	28.899	14.0
10	2	1	1	2.81700	31.738	100.0
11	1	1	2	2.77900	32.184	43.0
12	3	0	0	2.72300	32.864	55.0
13	2	0	2	2.63100	34.048	24.0
14	3	0	1	2.53200	35.422	4.0

15	2	1	2	2.29800	39.169	5.0
16	1	3	0	2.26500	39.763	20.0
17	2	2	1	2.23100	40.396	2.0
18	1	3	1	2.15200	41.947	5.0
19	1	1	3	2.06300	43.848	4.0
20	2	0	3	1.99990	45.307	3.0
21	2	2	2	1.94500	46.661	24.0
22	1	3	2	1.89210	48.046	12.0
23	2	3	0	1.87390	48.543	4.0
24	2	1	3	1.84120	49.462	26.0
25	3	2	1	1.80810	50.430	15.0
26	4	1	0	1.78250	51.206	10.0
27	4	0	2	1.75610	52.033	11.0
28	0	0	4	1.72020	53.203	12.0
29	3	2	2	1.64570	55.816	5.0
30	3	1	3	1.61180	57.097	3.0
31	2	4	0	1.54370	59.865	3.0
32	3	3	1	1.53250	60.348	3.0
33	2	4	1	1.50620	61.515	3.0
34	1	2	4	1.50270	61.674	4.0
35	5	0	2	1.47570	62.930	6.0
36	5	1	0	1.46710	63.341	2.0
37	3	0	4	1.45430	63.965	6.0
38	3	2	3	1.45120	64.117	7.0
39	5	1	1	1.43480	64.940	6.0
40	3	3	2	1.42980	65.195	4.0
41	4	1	3	1.40740	66.365	2.0
42	5	1	2	1.34950	69.611	2.0
43	4	3	1	1.31800	71.526	3.0
44	4	0	4	1.31560	71.676	2.0

45	5	2	0	1.30800	72.158	2.0
46	5	2	1	1.28500	73.660	2.0
47	2	4	3	1.28060	73.955	3.0
48	2	1	5	1.25700	75.583	4.0
49	3	4	2	1.25100	76.010	2.0
50	6	1	0	1.24570	76.392	2.0
51	1	4	4	1.23780	76.968	5.0
52	5	1	3	1.23590	77.108	4.0
53	6	1	1	1.22260	78.105	4.0
54	4	4	1	1.15890	83.313	3.0
55	2	4	4	1.14890	84.204	2.0
56	0	0	6	1.14680	84.393	2.0
57	5	1	4	1.11440	87.451	3.0
58	2	3	5	1.10920	87.966	2.0
59	3	5	2	1.10510	88.377	4.0
60	2	2	6	1.03130	96.645	2.0

Stick Pattern



Name and formula

Reference code: 00-002-1216

Mineral name: Bunsenite
PDF index name: Nickel Oxide

Empirical formula: NiO
Chemical formula: NiO

Crystallographic parameters

Crystal system: Cubic
Space group: Fm-3m
Space group number: 225

a (?): 4.1720
b (?): 4.1720
c (?): 4.1720
Alpha (?): 90.0000
Beta (?): 90.0000
Gamma (?): 90.0000

Measured density (g/cm^3): 6.80
Volume of cell (10^6 pm^3): 72.62
Z: 4.00

RIR: -

Status, subfiles and quality

Status:	Marked as deleted by ICDD
Subfiles:	Inorganic Mineral Alloy, metal or intermetalic
Quality:	Blank (B)

Comments

Deleted by:	Deleted by NBS card.
Color:	Green
Optical data:	B=2.37
Melting point:	1955

References

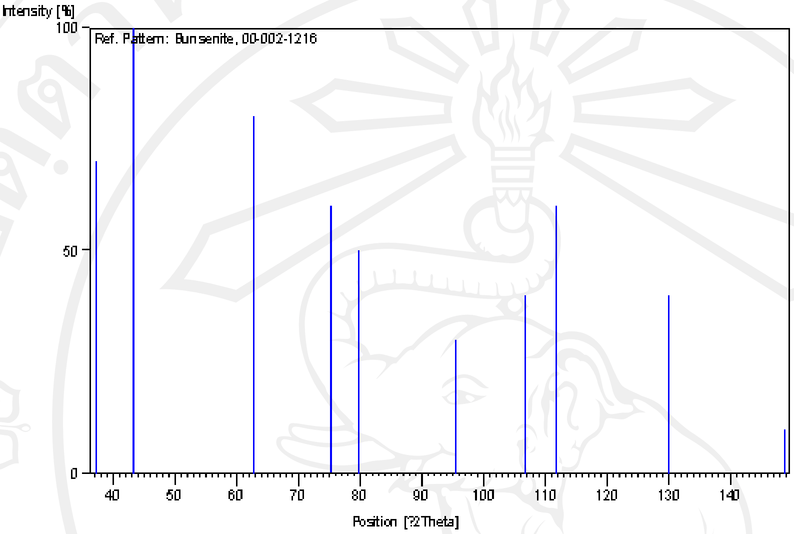
Primary reference:	Levi, Taccini., *Gazz. Chim. Ital.*, **55**, 30, (1925)
Additional pattern:	Jefferson, Shultz., *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **73**, 380, (1930)

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	1	1	2.41000	37.280	70.0
2	2	0	0	2.09000	43.253	100.0
3	2	2	0	1.48000	62.726	80.0
4	3	1	1	1.26000	75.372	60.0
5	2	2	2	1.20000	79.867	50.0
6	4	0	0	1.04000	95.574	30.0
7	3	3	1	0.96000	106.715	40.0
8	4	2	0	0.93000	111.840	60.0
9	4	2	2	0.85000	129.974	40.0

10	5	1	1	0.80000	148.667	10.0

Stick Pattern



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Biomaterials & Applications
(CMICBA 2011),
August 9-10, 2011, Chiang Mai, Thailand

Edited by

Tawee Tunkasiri

TTP

Advanced Materials Research Vol. 506 (2012) pp 234-237
© (2012) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/AMR.506.234

Effect of Metal Oxide Nano-particles Addition on Physical Properties of Hydroxyapatite

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Keywords: Hydroxyapatite; Bioceramic, Metal Oxide,

Abstract. In the present study the effects of metal oxide nano-particles addition on the microstructure, physical properties of the HA ceramics were investigated. Many techniques were used for the analysis. X-ray diffraction analysis revealed a co-exist phases between hydroxyapatite and tricalcium phosphate in the sintered samples. Addition of NiO resulted an increase in the lattice parameters of the tricalcium phosphates due to the bigger radii atom (Ni) substitution for the small radii atom (Ca). Energy dispersive spectroscopy suggested that most of NiO particles located at grain boundary, resulting in an improvement of hardness of the samples

Introduction

Hydroxyapatite (HA) is a class of calcium phosphate-based bioceramic materials which has chemical formula [$Ca_{10}(PO_4)_6(OH)_2$] with calcium and phosphate molar ratio of 1.67. This material frequently used in the biomedical field because of their excellent biocompatibility and their bio-component being similar to natural bone and teeth of the human body [1]. However, their brittle and low fracture toughness limit their biomedical used especially for loading applications [2]. Therefore, there have been many attempts to improve the mechanical and physical properties of sintered HA [1, 3, 4].

To synthesis HA, many approaches have been proposed such as hydrothermal method [5], continuous precipitation [6] and solid state reaction method [5]. Further, HA can derive from natural sources such as natural calcite [8] and bovine bone[9]. Many investigations on HA also have concentrated on a wide range of powder processing techniques, composition and experimental conditions with the aim of determining the most viable synthesis method and conditions to produce well-defined particle morphology. It is reported that the sintering temperature and atmosphere are important factors that could alter the strength and toughness of HA [10]. Sintering at high temperatures also has the tendency to eliminate the functional group OH in the HA matrix and this would result in the decomposition of HA phase to form α-tricalcium phosphate (α-TCP), β-tricalcium phosphate (β-TCP) and tetracalcium phosphate (TTCP) [10]. The formation of these phases affects to the mechanical properties of HA ceramics[11]. Further, the influence of additives on the properties has been reported. The additives also affect to the properties of the HA ceramics. The present work aimed to study effects of metal oxide nano-particle on physical and mechanical properties of HA ceramics. A nanocomposites between HA and NiO nano-particle were fabricated.

Experimental procedures

1. Sample preparation

The hydroxyapatite powder was derived from natural bovine bone by a sequence of thermal processes. The fresh bovine bones in all parts of one cow were cut into smaller pieces and cleaned well to remove macroscopic adhering impurities. The bone samples were boiled in distilled water for 8 h for easy removal of the bone marrow and tendons. After that the bones were de-proteinized by continued boiling in water. The boiled bone samples were dried overnight at a temperature of 200°C, thereafter was placed in sealed alumina crucibles and heated at temperatures about 800°C for 3 hours at a heating rate of 100°C/h and cooling rate of 300°C/h. The bones were grinded to a fine powder by a ball mill for 24 hours in the medium of ethanol and then dried at 110°C for 24 hours. Nickel oxide nano-partical (SIGMA-ALDRICH, 99.8%) was added to the bone powder in ratios of between 1 and 3 vol.%. The bone –NiO mixture, was ball-milled in isopropanol for 24 h using zirconia grinding media, then dried at 110°C for 12 h. The obtained powder was pressed into a disc shape and then sintered at 1325°C for 2 h.

2. Characterization

The density of the sintering HA disk was determined by using Archimedes method. Phase analysis by X-ray diffraction (XRD) of sintered HA was carried out at the room temperature. The crystalline phase compositions were identified with reference JCPDS data available in the system software. The microstructure of the samples was examined by scanning electron microscopy (SEM). All samples were sputter-coated with gold before the SEM examination. Chemical analysis and the distribution of NiO was also carried out using energy dispersive spectroscopy (EDS). For mechanical study, Vickers hardness was performed on polished surface using a microhardness testers.

Results and Discussion

The XRD patterns of pure HA and HA doped NiO nano-particals ceramics are showed in Fig.1. All the XRD patterns obtained for the samples were in agreement with the stoichiometric HA. The analysis was carried out based on the basis of Joint Committee on Powder Diffraction Standard (JCPDS) data file No. 01-086-1199. However, there was observed other phases in the samples, i.e. α-tricalcium phosphate (α-TCP) and β-tricalcium phosphate (β-TCP) characterized by JCPDS file No. 00-009-0348 and 00-009-0169, respectively. A similar result was also found by Ruksudjarit *et al.* [12] who prepared HA by vibro-milling method, suggesting that pure HA unstable at high temperatures (>1325 °C) [11]. It should be noted that the NiO-doped samples showed a shift in the α- TCP and β-TCP XRD peaks to lower Bragg's angles while NiO did not affect on the HA XRD peak position. This result suggested that some part of NiO has incorporation to α- TCP and β-TCP lattices. This thus can make an increase in the lattice parameters of α- TCP and β-TCP due to the bigger radii atom (Ni) substitution for the small radii atom (Ca).

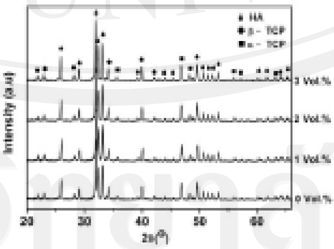

Fig. 1 XRD pattern of the hydroxyapatite sintering at 1325 °C.

The measured density data of the HA ceramics is listed in the Table 1. Density values were ~93- 95 %. To obtain better densification, higher sintering temperatures or longer soaking time would be required for further work. With increasing percent of NiO, the bulk density increased. This may be due the NiO has higher density than HA as a result in an increased in total density of the composites. The microstructures of HA ceramics, as revealed by the sintered surfaces, are shown in Fig. 2. Many micro-pores were observed in pure HA ceramic while 3 vol.% NiO-doped sample showed a dense structure with a monomodal grain size distribution. The microstructure also showed equiaxed grain shape. Therefore, the average grain size can be reasonably estimated by using the linear intercept method. The average grain size values are listed in Table 1. It was found that grain size unchanged with increasing the NiO content. In addition, EDS analysis suggested that most of NiO particles located at grain boundary.

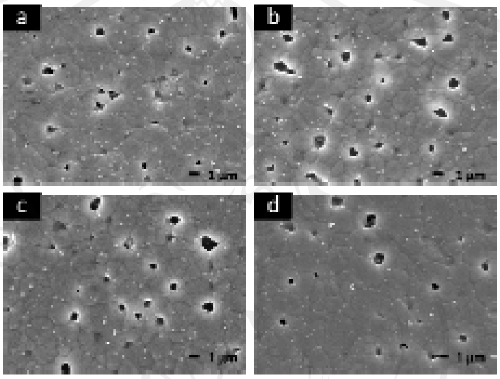

Fig. 2 SEM images of (a) pure HA, (b) added with 1Vol. % NiO, (c) added with 2 Vol. % NiO, (d) added with 3 Vol. % NiO

Table 1. Physical properties of hydroxyapatite ceramics

NiO doped(Vol. %)	Bulk densityg/ cm^3 (%)	Grain size(μm)	VickersHardness(GPa)
0	2.92(93.2)	1.49	5.50±0.05
1	2.94(93.9)	1.32	5.83±0.06
2	2.95(94.3)	1.35	5.83±0.15
3	2.97(95.0)	1.37	5.84±0.03

The variation of the average hardness of sample sintered at 1325°C is showed in Table 1. The hardness value increased from 5.50 GPa for the pure HA sample to 5.84 GPa for the 3 Vol.% doped sample. Therefore, the hardness was improved by adding the NiO nano-particle. The enhancement in hardness maybe due to the nanoparticles reinforced the grain boundaries. Further, density may also contribute to the improvement, i.e. the higher density gave higher measured hardness value.

Conclusions

The new composites between HA and NiO nano-particles were fabricated in the present work. Properties of the composites were investigated by variety techniques. XRD analysis suggested that NiO nano-particles affected densification and phase formation. Most of NiO nano-particles located at grain boundary, identified by EDS analysis. This characteristic can thus connect to the improvement of mechanical property of the composites.

Acknowledgements

The authors would like to thank Thailand Research Fund (FRT),National Metal and Materials technology center, Office of the Higher Education Commission (OHEC), Faculty of Science and the Graduate school, Chiang Mai University, Thailand of financial support.

References

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ผลงานวิจัย	**Publication** N. Lertcumfu, P.Jararupoom, K. Pemgpat, T. Tunkasiri, G.Rujijanagul, Effect of Metel Oxide Nano-particles Addition on Physical Properties of Hydroxyapatite, Advanced Materials Research 506, (2012) 234-237.