

HA powders calcined at 1000°C were dry-mixed in an agate mortar with potassium sulfate ( $K_2SO_4$ , 99.9% purity, Merck) at weight of 2 g. In several experiments, the  $K_2SO_4$  (melting point  $MP = 1069^\circ C$ ) flux was replaced by sodium sulfate ( $Na_2SO_4$ ,  $MP = 884^\circ C$ ), calcium chloride ( $CaCl_2$ ,  $MP = 782^\circ C$ ), potassium chloride ( $KCl$ ,  $MP = 771^\circ C$ ), or potassium bromide (KBr,  $MP = 734^\circ C$ ). The mixtures, as loose powder compacts, were then placed into clean alumina boats with a volume of  $7.5\text{ cm}^3$  and set inside a box furnace. The samples were heated from the ambient to the peak temperature of whisker synthesis at a rate of  $5^\circ C/min$ . Following soaking times ranging from 0.5 to 3.5 h at the peak temperatures ( $850^\circ C$ – $1190^\circ C$ ), the samples were cooled naturally to room temperature within the shut-off furnace. The single-crystal whiskers or particles were separated from the solidified mass by washing the mass several times with hot ( $\sim 90^\circ C$ ) deionized water.

(2) Synthesis of HA Whiskers

The single-phase calcium hydroxyapatite powders used as the starting material for the MSS of the HA whiskers were synthesized as follows.<sup>23–25</sup> The following procedure is the derivative of a route described earlier by Hayek and Newesely,<sup>26</sup> Moreno *et al.*,<sup>27</sup> and Jarcho *et al.*<sup>28</sup> A 3 mL aliquot of 0.1 g/L methyl cellulose solution (99% purity, Sigma-Aldrich Corp., St. Louis, MO) was mixed (to act as a dispersant) with 1440 mL of deionized water. Next, 0.152 mol of  $Ca(NO_3)_2 \cdot 4H_2O$  (99.8% purity, Merck, Darmstadt, Germany) was dissolved in the above-described solution. Then, 0.090 mol of  $(NH_4)_2HPO_4$  (99.8% purity, Merck) was dissolved in that solution. Following that step, 115 mL of 24 vol%  $NH_4OH$  was added, in its entirety, to the above-described opaque solution. The solution was heated and vigorously stirred at  $60^\circ C$ – $70^\circ C$  for 3 h, on a hot plate. The precipitates that formed were recovered from the supernatant, by filtering, and washed five times with deionized water. The filtrates were dried at  $100^\circ C$  overnight. Finally, the HA precursors were calcined in an air atmosphere at  $1000^\circ C$  for 6 h and then highly ground by hand, with an agate mortar and pestle.

(1) Preparation of HA Powders

II. Experimental Procedure

In the present study, we used submicrometer-sized HA powders synthesized by a previous method<sup>23–25</sup> as the starting material for the MSS method. The effects on whisker morphology of the alkali salt chosen, the temperatures/times of synthesis, and the salt-to-HA powder ratio used were studied. To our knowledge, this report is the first describing the successful preparation of mono-disperse HA whiskers, using  $K_2SO_4$  salt, by the simple technique of MSS.

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Molten Salt Synthesis of Calcium Hydroxyapatite Whiskers

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Calcium hydroxyapatite (HA) whiskers and crystals were produced by the route of molten salt synthesis. The effects on whisker morphology of chosen flux, flux-to-HA ratio, synthesis temperature, and reaction time were investigated. The thermal stabilities of the produced whiskers were tested at  $1300^\circ C$  in an atmosphere. A tentative X-ray diffraction pattern was proposed for the HA whiskers. Molten salt synthesis with a  $K_2SO_4$  flux was found to be a simple and sturdy technique for manufacturing short ( $\leq 60\ \mu m$ ) HA whiskers in the temperature range from  $1080^\circ C$  to  $\sim 1200^\circ C$ . The alternative use of fluxes such as KCl, KBr,  $CaCl_2$ , or  $Na_2SO_4$ , rather than  $K_2SO_4$ , over the temperature range  $850^\circ C$ – $1000^\circ C$  resulted in the formation of large ( $\sim 25\ \mu m$ ) single crystals of HA.

I. Introduction

Calcium hydroxyapatite ( $Ca_{10}(PO_4)_6(OH)_2$ ) is one of the most biocompatible ceramics, because of its significant chemical and physical resemblance to the mineral constituents of human teeth. For load-bearing orthopedic and dental applications, densified HA ceramics are needed. However, dense HA ceramics manufactured by using synthetic HA powders have always exhibited a low fracture toughness, of  $\sim 1\text{ MPa}\cdot m^{1/2}$ , in contrast to the values observed for human bones, in the range  $10$ – $20\text{ MPa}\cdot m^{1/2}$ .<sup>1</sup> Reinforcement by whiskers has been considered as a way of improving the fracture toughness of pure HA bioceramics; thus, whisker-like or needlelike crystals of HA have been synthesized in years, mainly by the hydrothermal method or precipitation.<sup>2–9</sup> However, the whiskers synthesized by these methods<sup>4–6</sup> suffer from nonstoichiometry (i.e., calcium deficiency) and have poor thermal stability, i.e., they partially decompose into a  $\beta$ -TCP phase ( $5$ – $35\text{ vol}\%$  TCP), even after 1 h of heating at  $1100^\circ C$ .<sup>10</sup> Suchanek *et al.*<sup>5</sup> have reported that, for HA composite matrices reinforced with hydrothermally synthesized HA whiskers ( $10$ – $30\text{ vol}\%$  whiskers), the whiskers disappear within the HA matrices at sintering temperatures  $\geq 1000^\circ C$  and turn themselves into large, equiaxed grains.<sup>9</sup> The fracture toughness values of these samples have been reported<sup>7</sup> to remain only in the modest range of  $1$ – $2\text{ MPa}\cdot m^{1/2}$ .<sup>12</sup> Molten salt synthesis (MSS) is reported to be one of the most effective techniques for preparing ceramic powder bodies with needlelike, needlelike, or plate-like morphology and, as well, complex stoichiometry.<sup>10</sup> The MSS technique is based on the use of low-melting solvents, such as alkali chlorides, sulfates, carbonates, or hydroxides, as the medium of reaction for the ceramics. The literature on molten salt synthesis is quite extensive and, to date, not a few cases, this technique has been used (with different salts) to prepare ferrites,<sup>10</sup> titanates,<sup>11–13</sup> niobates,<sup>14–17</sup>

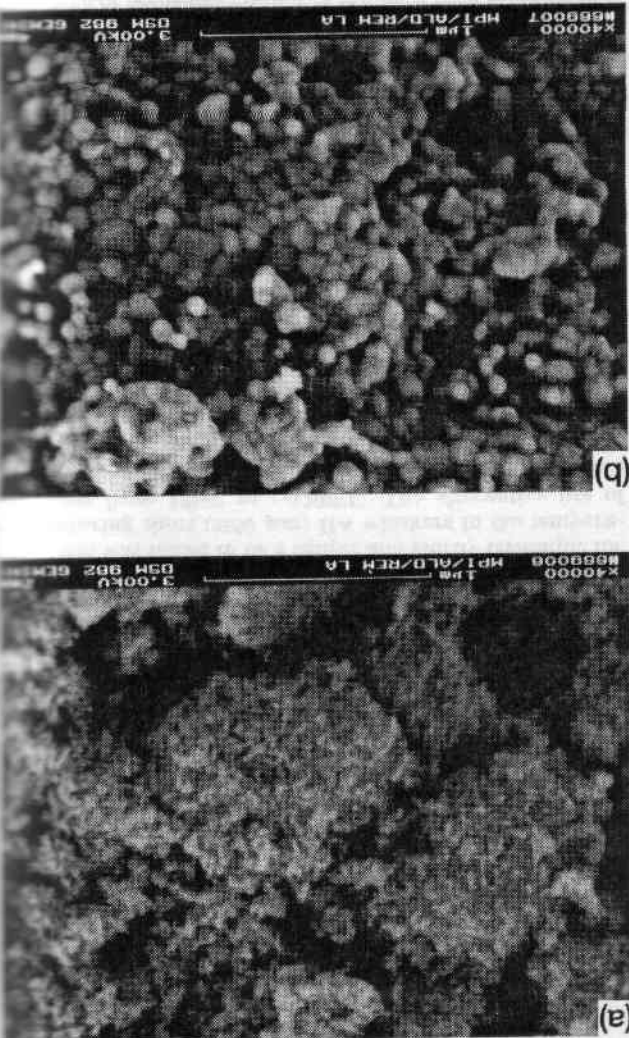
The lattice parameters of the W4 whiskers (middle XRD trace in Fig. 2) were determined, by least-squares analysis,<sup>29</sup> to be  $a = 9.4189$  and  $c = 6.8827$  Å. The hexagonal unit cell (of the space group of  $P6_3/m$ ) had a cell volume of  $528.79$  Å<sup>3</sup>. The lattice parameters of these whiskers resembled those reported previously<sup>30</sup> for the apatite of human bones, although these whiskers and human bones do not have the same chemical constitution. The

However, human bones and tooth enamel are also known to contain significant quantities of alkali and alkali earth cations, such as Na<sup>+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup>. The sum of these three ions in human bones reaches  $\sim 1.3$  wt%, whereas, in enamels, the same figure has been reported<sup>30</sup> to be  $\sim 1$  wt%. On the other hand, the Ca/P molar ratio of the present MSS whiskers was found, by ICP-AES analyses, to be  $1.64 \pm 0.01$ . These whiskers may also be regarded as calcium-deficient, in comparison with stoichiometric HA, which has a Ca/P molar ratio of 1.667. However, the Ca/P ratios of dental enamel and human bones are known<sup>30</sup> to be 1.62 and 1.65, respectively.

The SEM micrographs of the W4 whiskers (middle XRD trace in Fig. 2) were determined, by least-squares analysis,<sup>29</sup> to be  $a = 9.4189$  and  $c = 6.8827$  Å. The hexagonal unit cell (of the space group of  $P6_3/m$ ) had a cell volume of  $528.79$  Å<sup>3</sup>. The lattice parameters of these whiskers resembled those reported previously<sup>30</sup> for the apatite of human bones, although these whiskers and human bones do not have the same chemical constitution. The

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Fig. 1. SEM micrographs of HA powders at (a) 100°C and (b) 1000°C.



The SEM micrographs given in Fig. 1 show the morphology of the starting HA powders used in this study in molten salt whisker synthesis. The chemically precipitated HA precursors, following filtration from the mother liquor and 100°C drying, consisted of nanosized, but aggregated, particles, as depicted in Fig. 1(a). These precursors were poorly crystalline, but not completely amorphous. Their crystallization behavior, as a function of calcination temperature, has been published elsewhere.<sup>25</sup> Figure 1(b) shows the microstructure of the same powders after calcination (as a loose powder compact) in air at 1000°C for 6 h. The average particle size was  $\sim 100$  nm. Calculated HA powders were determined, by XRD, to be "single-phase" HA (with only a small amount of CaO, not readily detectable by rapid XRD scans) with a Ca/P atomic ratio (measured by ICP-AES) of  $1.68 \pm 0.01$ .<sup>24,25</sup> This Ca/P ratio in the calcined powders was intentionally adjusted to that value by the specific Ca/P ratio used in the chemical precipitation of precursors. The XRD pattern of the calcined (1000°C, 6 h) HA powders is shown as the bottom trace of Fig. 2.

HA powders precipitated at 1000°C (to ensure that the starting materials consisted of single-phase hydroxyapatite) were then mixed with the alkali salts listed in Table I for MSS,  $K_2SO_4$  was first<sup>29</sup> tested as the fusing agent in MSS runs at four different salt-to-HA weight ratios and four different temperatures. The samples, labeled W1-W12 (see Table I), all produced single-phase HA whiskers. The XRD pattern of the W4 sample is shown by the middle trace of Fig. 2. The same XRD trace was observed for all of the samples, labeled as W1 in Table I. That trace represents the characteristic XRD pattern for calcium hydroxyapatite, although the intensities of the 211 and 300 planes are changed, because of whisker orientation. This result was also the case for previously reported<sup>23,26</sup> hydrothermally synthesized HA whiskers, and the whiskers were apparently elongated along the c axis. Moreover, all of the HA whiskers of samples W1-W12 were totally transparent, according to examination by optical microscopy.

### III. Results and Discussion

The phase constitution of the whiskers was analyzed by XRD (Model No. D-5000, Siemens Aktengesellschaft, Karlsruhe, Germany) and CuK $\alpha$  radiation (40 kV, 30 mA). For lattice-parameter determinations, a scan rate of  $0.2^\circ/2\theta$  min (over the range  $10^\circ-70^\circ 2\theta$ ), using a silicon external standard to correct for systematic errors, was used, along with the Appelman Least-Squares Refinement Program.<sup>27</sup> The morphologic and semiquantitative elemental distribution information on the samples were obtained by SEM (Model No. DSM 982-German, Karl Zeiss, Inc., Oberkochen, Germany), and by energy dispersive X-ray spectroscopy (EDS), respectively. Quantitative elemental analyses were performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Model No. JV-70Plus, Jobin Yvon S.A., Longjumeau, France). An FT-IR spectrophotometer (Model No. IFS66, Bruker, Karlsruhe, Germany) was used to measure the infrared transmission spectra of the whiskers, after the whiskers had been mixed with dry KBr (1 wt%), to form pellets.

#### (4) Sample Characterization

The morphology and phase stability of the HA whiskers after heating (with heating/cooling rates of  $5^\circ/\text{min}$ ) at 1300°C for 9 h, as a loose powder compact, in an air atmosphere, were evaluated by scanning electron microscopy (SEM), X-ray diffractometry (XRD), and Fourier transform infrared spectroscopy (FT-IR).

#### (3) Investigation of Thermal Stability of Whiskers

Washing was repeated until the specific conductance of the decanted liquid fell to  $<2.4$   $\mu\text{S}$ , measured<sup>1</sup> using a conductance meter (Model No. Dtg1610, WTW, Weilheim, Germany), knowing that the conductance of deionized water was 1.4  $\mu\text{S}$ . Finally, the washed whiskers were dried in an oven, at 100°C, overnight.

presence of  $K^+$  in the lattice also has been reported previously<sup>30</sup> to have no influence on the lattice parameters of hydroxyapatite. Therefore, a tentative XRD pattern for the HA whiskers (with the strongest XRD peak assigned to the 300, rather than the 211, plane) was created and is given in Table II. Figures 3(a) and (b) show the SEM micrographs of molten-salt-synthesized HA whiskers of samples W1 and W4, respectively. The aspect ratios (i.e., length/diameter) varied in the range 2–18, with the median whisker diameter and length 9  $\mu\text{m}$  and 55  $\mu\text{m}$ , respectively. Whiskers were monodisperse and were not fused to one another. Interestingly, samples W2, W3, and W5–W11 produced almost the same microstructures and whisker morphologies. Thus, the  $K_2\text{SO}_4$ -to-HA weight ratio (in the range 1.2–3.0), the reaction temperature (in the range 1100–1190°C), and the reaction time (in the range 1–3.5 h) were almost unable to influence the resultant HA whisker morphology. On the other hand, Fig. 3(c) shows that sample W12 (i.e., 1080°C, 0.5 h,  $K_2\text{SO}_4$ -to-HA weight ratio = 3.0) exhibited the formation of monodisperse, but much thinner, HA whiskers, with an aspect ratio >30 and a typical diameter and length of 2  $\mu\text{m}$  and 65  $\mu\text{m}$ , respectively. The XRD

Sample	Salt	Salt/HA (by weight)	Reaction temperature (°C)	Reaction time (h)
W1	$K_2\text{SO}_4$	1.2	1190	3.5
W2	$K_2\text{SO}_4$	1.2	1150	2.0
W3	$K_2\text{SO}_4$	1.2	1100	1.0
W4	$K_2\text{SO}_4$	1.6	1190	3.5
W5	$K_2\text{SO}_4$	1.6	1150	2.0
W6	$K_2\text{SO}_4$	3.0	1190	3.5
W7	$K_2\text{SO}_4$	2.4	1190	3.5
W8	$K_2\text{SO}_4$	3.0	1190	3.5
W9	$K_2\text{SO}_4$	3.0	1150	2.0
W10	$K_2\text{SO}_4$	3.0	1100	2.0
W11	$K_2\text{SO}_4$	3.0	1100	1.0
W12	$K_2\text{SO}_4$	3.0	1080	0.5
W1	KCl	1.6	880	3.0
W2	KCl	1.6	1000	3.0
W3	KBr	1.6	1000	3.0
W4	KBr	1.6	1000	3.0
W5	$\text{Na}_2\text{SO}_4$	3.0	1000	3.0
W6	$\text{CaCl}_2$	3.0	850	3.0
W7	$\text{CaCl}_2$	3.0	1000	3.0

Table I. Molten-Salt-Synthesized Samples

Fig. 2. XRD patterns of HA powders and whiskers.

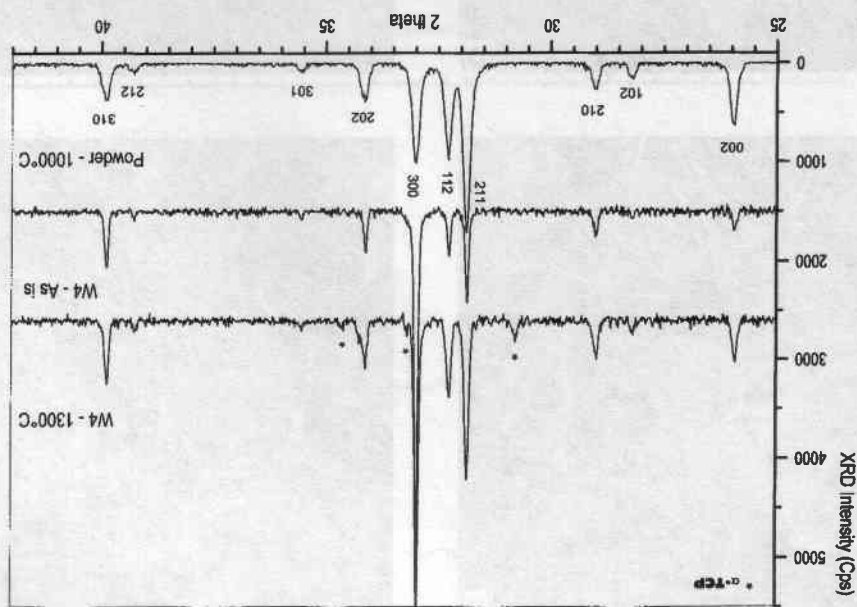


Table II. Experimental XRD Pattern of HA Whiskers†

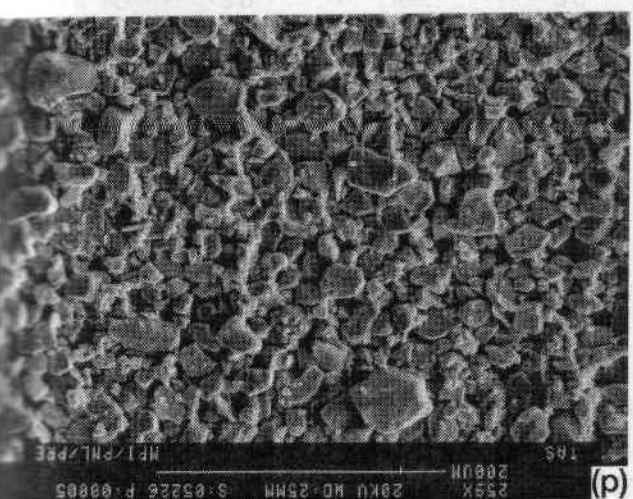
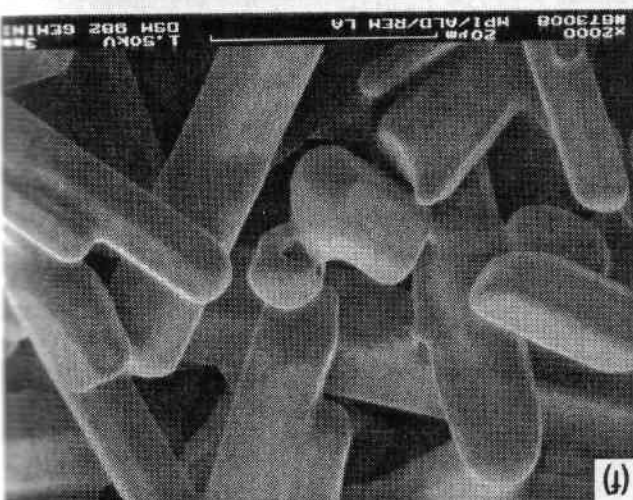
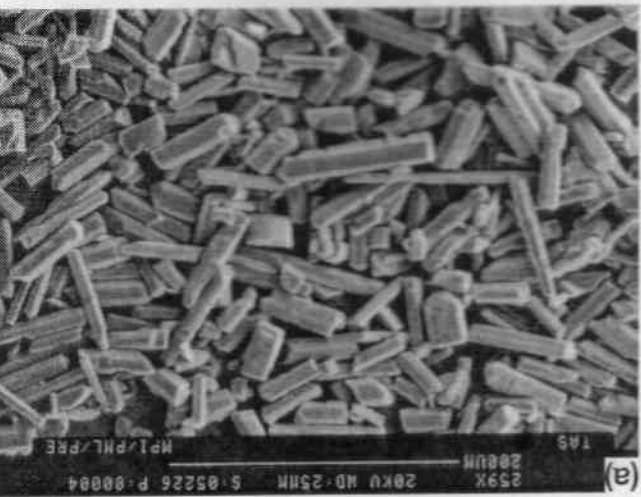
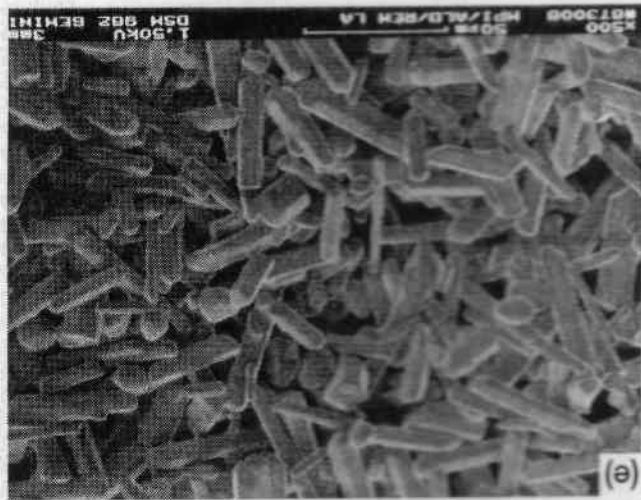
$2\theta$	$d$ (Å)	$hkl$	$h^2 + k^2 + l^2$
10.8335	8.1600	100	8
16.8416	5.2601	101	4
18.8287	4.7092	110	3
21.7654	4.0800	200	9
22.8615	3.8868	111	8
25.8647	3.4419	002	7
28.1278	3.1699	102	2
28.9355	3.0832	210	8
31.7870	2.8128	211	26
32.1873	2.7788	112	13
32.9093	2.7194	300	100
34.0553	2.6305	202	12
35.4751	2.5284	301	3
39.1983	2.2964	212	3
39.8151	2.2622	310	18
42.3272	2.1492	311	2
42.3272	2.1492	302	3
43.8628	2.0624	113	6
44.3859	2.0393	400	3
45.3132	1.9997	203	2
46.7025	1.9434	222	9
48.0899	1.8905	312	4
48.6156	1.8713	320	3
49.4793	1.8406	213	9
50.5031	1.8057	321	6
51.2834	1.7800	410	9
52.0951	1.7542	402	4
53.1910	1.7206	004	3
54.4593	1.6835	104	3
55.8807	1.6440	322	7
57.1331	1.6109	313	5
58.0628	1.5873	501	2
59.9570	1.5416	420	3
60.4326	1.5306	331	3
61.6848	1.5025	214	7
63.0029	1.4742	502	2
63.4444	1.4650	510	2
64.1687	1.4502	323	6
65.0382	1.4329	511	2
66.3987	1.4068	422	2
69.7071	1.3479	512	1

† For W4 at 1190°C.

pattern of this sample again showed the presence of calcium hydroxyapatite only.  
 The above set of experimental data, obtained using  $K_2SO_4$  as the fluxing agent, implies the following process:  
 (1) The liquid phase formed during the MSS process by the molten  $K_2SO_4$  (i.e., the flux) first dissolves all of the initial ceramic raw material.  
 (2) With further heating, particles of the apatite phase are formed through the nucleation and growth processes.<sup>16</sup>

(3) As the molten ionic bath cools, while passing through its melting point down to room temperature, rapid crystallization occurs along the preferred growth axes of the ceramic phase.  
 (4) HA whisker growth occurs during MSS, by a sequential "dissolution-crystallization-whisker-growth" process.  
 (5) Solubility of the ceramic raw material in the molten flux (which is a function of temperature) must have a significant role in the crystallization process to follow.

Fig. 3. SEM micrographs of HA whiskers and crystals: (a) W1, (b) W4, (c) W12, (d) P1, (e) and (f) W4 at 1300°C (see Table I for sample designations).



Molten salt synthesis (MSS) of monodisperse calcium hydroxyapatite whiskers was accomplished using a  $K_2SO_4$  flux. Single-phase, potassium-doped HA whiskers proved possible to synthesize over the temperature range 1080–1190°C, and the  $K_2SO_4$ -to-HA ratios in the initial mixtures could be varied between 1.2 and 3.0 without significantly affecting the whisker morphology.

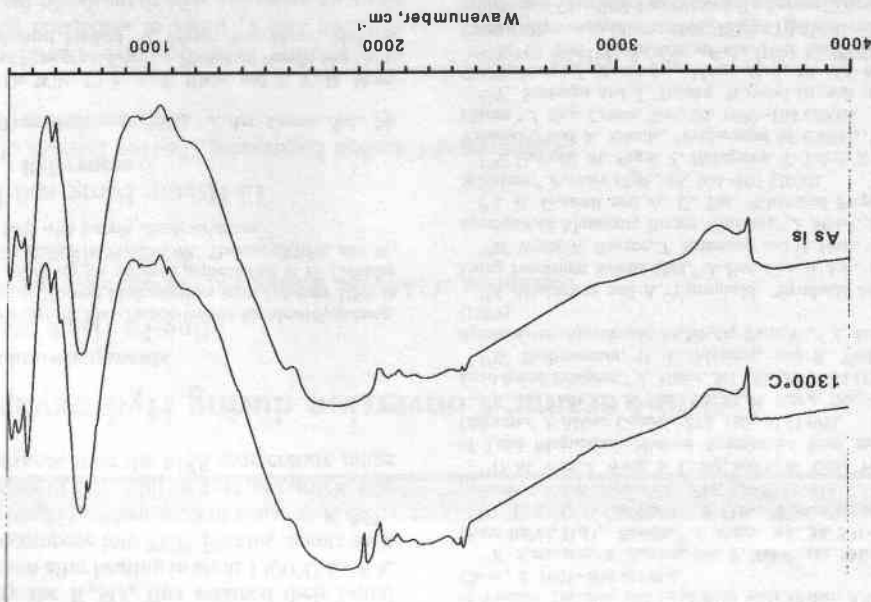
#### IV. Summary

Biocompatible HA whiskers prepared by the MSS technique could be useful for numerous applications involving the reinforcement of hydroxyapatite-based bioceramics. As shown in this report, the MSS process for calcium hydroxyapatite whisker manufacture is quite robust, because it does not require the achievement of precise, up-to-the-last-digit control over many of the processing parameters, such as the flux-to-HA ratio, reaction temperature, and time.

The infrared spectrum of the W4 whiskers calcined in air at 1300°C for 9 h (depicted by the top trace in Fig. 4) shows, as well as all of the above-mentioned bands, a unique band at 743  $cm^{-1}$ , which is characteristic of the P-O-P vibrational mode of pyrophosphates,<sup>32</sup> although their XRD patterns did not indicate the presence of  $Ca_2P_2O_7$  as a decomposition product. The band at 1933  $cm^{-1}$  could not be identified.

The FT-IR spectrum of the as-synthesized W4 whiskers shown in the bottom trace of Fig. 4 is characteristic for calcium hydroxyapatite. All bands originating from  $PO_4$  and OH groups are clearly visible. The absence of any distinct bands in the range 1500–1400  $cm^{-1}$  means that the HA whiskers do not contain significant quantities of carbonate ions.<sup>32</sup> Bands in the region 1190–975  $cm^{-1}$  result from the  $\nu_3$  vibrational mode of the phosphate group. A phosphate  $\nu_4$  band is present at ~962  $cm^{-1}$ . A phosphate  $\nu_2$  band is present in the region 605–560  $cm^{-1}$ , and two sites are observed for these whiskers at 602 and 569  $cm^{-1}$ . A phosphate vibration,  $\nu_2$ , is observed in the form of two discrete peaks at 471 and 433  $cm^{-1}$ . The OH vibrations at 3571  $cm^{-1}$  (stretching) and 634  $cm^{-1}$  (bending) are well-defined, and the band in the region 1638–1600  $cm^{-1}$  is a result of H-O-H deformation. Atmospheric  $CO_2$  is indicated by the band at 2349  $cm^{-1}$ .

Fig. 4. FT-IR spectra (transmittance) of HA whiskers.



The extent of superheating of the molten flux must also rather strong effect on the resultant aspect ratio of the whiskers (as evidenced by the case of sample W12). The morphology of the whiskers growing out of the molten salt bath must be strongly dependent on soaking time at the peak temperature.

Whiskers with the highest aspect ratio were obtained at the temperature and time combination, i.e., sample W12 of Table I. A result suggesting that time and temperature are the most significant variables in altering the whisker morphology, along with the use of an appropriate fluxing agent, in which the ceramic material has sufficient solubility.

To test the feasibility of decreasing the MSS temperature, we tried using KCl, KBr,  $Na_2SO_4$ , and  $CaCl_2$ , rather than  $K_2SO_4$ , with the MSS parameters given in Table I. These samples were labeled P1–P7. Interestingly, none of the samples were able to produce HA whiskers, and the reason(s) for this failure may also be found in the above paragraph. Figure 3(d) shows the SEM micrograph of the P1 powders, and this morphology was also encountered with the other samples, P2–P7. The product phase in all of these samples was, again, calcium hydroxyapatite, with an average particle size of 25  $\mu m$ . The finer portion of the powder body (or Fig. 3(d)) is believed to have been the undissolved, initial HA powder, and the finer portion consisted of single crystals of HA. Such hydroxyapatite whiskers, with a large average particle size, may be useful for applications such as plasma-spraying. However, ICP-AES analyses determined on the P1 and P2 samples indicated the presence of KCl (in the range 1.5%–1.7%) in the final powders. It can be assumed that using KCl as the molten salt facilitates at least the partial transformation of hydroxyapatite into chlorapatite.

Figures 3(e) and (f) show the microstructures of W4 whiskers at different magnifications, after heating as loose powder contained in alumina boats, at 1300°C, for 9 h in a stagnant air atmosphere. For the molten-salt-synthesized HA whiskers of the present study, the previously mentioned problem (for the whiskers characterized by the hydrothermal method)<sup>3–6</sup> of morphology degradation apparently was not present. The W4 whiskers retained their shapes perfectly, formed a skeleton of HA, and just fused together at the points of mutual contact. However, the XRD pattern of the whiskers heated at 1300°C (see Fig. 2) showed the presence of a second phase of  $\alpha$ -TCP (ICDD No. PDF 9–348), the

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HA whiskers produced by the  $K_2SO_4$  flux retained their initial shapes and aspect ratios, even after heating in air at 1300°C for 9 h, although they started to decompose into TCP. Fluxing agents such as KCl, KBr,  $CaCl_2$ , and  $Na_2SO_4$  when used in place of  $K_2SO_4$  produced large, rather than whiskers, over the MSS temperature range of 25  $\mu m$ , rather than whiskers, over the MSS temperature range 850–1000°C.

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**References**

1. L. Heale, "Evaporation from Gels to Cracks," *J. Am. Ceram. Soc.*, **74**, 1437–510 (1991).

2. Y. Yoda, K. Ito, G. H. Kim, and S. V. D. Meer, "Micrograph and Comparison of Nanoparticle Calcium Phosphate Needle-like Crystals Formed by Simple Hydrothermal Method," *J. Mater. Sci., Mater. Med.*, **5**, 326–31 (1994).

3. M. Yoshimura, H. Sato, K. Harano, and K. Kikkawa, "Hydrothermal Synthesis of Bioceramic Whiskers," *J. Mater. Sci.*, **29**, 399–402 (1994).

4. W. Saitoh, H. Sato, M. Kubota, and M. Yoshimura, "Bioceramic Whiskers with Controlled Morphology and Stoichiometry," *J. Mater. Res.*, **10**, 221–29 (1995).

5. W. Saitoh, M. Kubota, M. Yoshimura, and M. Yoshimura, "Hydroxyapatite Hydroxyapatite Whisker Composites without Sintering Additives: Mechanical Properties and Microstructural Examination," *J. Am. Ceram. Soc.*, **80**, 2805–13 (1997).

6. W. Saitoh and M. Yoshimura, "Preparation of Fibrous, Porous Hydroxyapatite Composites from Hydroxyapatite Whiskers," *J. Am. Ceram. Soc.*, **81**, 765–67 (1998).

7. T. Endo and A. Nishida, "Effects of pH of the Aqueous Solutions on the Growth of Hydroxyapatite Whiskers," *J. Ceram. Soc. Jpn.*, **106**, 820–23 (1998).

8. T. Endo and A. Nishida, "Effects of the Buffer Solutions on the Growth of Hydroxyapatite Whiskers," *J. Ceram. Soc. Jpn.*, **107**, 442–48 (1999).

9. A. Nishida, M. Saitoh, S. Yamaguchi, M. Kaneno, S. Takeda, and M. Yoshimura, "New Synthetic Method of Hydroxyapatite Whiskers by Hydrolysis of  $\alpha$ -Tricalcium Phosphate in Mixtures of Water and Organic Solvent," *J. Am. Ceram. Soc.*, **82**, 2029–32 (1999).

10. R. H. Kramo, "The Modern Sol Synthesis of Single Magnetic Domain  $BaFe_{12}O_{19}$  and  $SrFe_{12}O_{19}$  Crystals," *J. Solid State Chem.*, **8**, 339–47 (1973).

11. P. A. Fournier and R. E. Newkome, "La, Ti, O<sub>2</sub> Ceramics," *J. Am. Ceram. Soc.*, **74**, 2575–81 (1991).

12. A. Aboumout, L. P. Lecomte, F. Chasseigneux, J. P. Scharff, and B. Durand, "Molten Salt Synthesis of the Lead Titanate  $PbTiO_3$ , Investigation of the Reactivity

of Various Titanium and Lead Salts with Molten Alkali-Metal Nitrates," *J. Mater. Chem.*, **8**, 1601–606 (1998).

13. K. Katayama, Y. Azuma, and Y. Takahashi, "Molten Salt Synthesis of  $SrFe_{12}O_{19}$  Phase  $BaNd_{2}Ti_{12}O_{32}$  Powder," *J. Mater. Sci.*, **34**, 301–305 (1999).

14. C. Li, C. C. Chiu, and S. B. Desu, "Formation of Lead Niobates in Molten Systems," *J. Am. Ceram. Soc.*, **74**, 42–47 (1991).

15. D. M. Wan, J. Wang, S. C. Ng, and L. M. Gan, "Formation and Characterization of Lead Magnesium Niobate Synthesized from the Molten Salt of Potassium Chlorate," *J. Alloys Compd.*, **274**, 110–17 (1998).

16. K. H. Yoon, Y. S. Cho, and D. H. Kang, "Review: Molten Salt Synthesis of Lead-based Relaxors," *J. Mater. Sci.*, **33**, 297–84 (1998).

17. B. Brahmanouli, G. L. Messing, and S. Trolier-McKinstry, "Molten Salt Synthesis of Antiferroelectric  $Sr_{2}Nb_{2}O_{7}$  Particles," *J. Am. Ceram. Soc.*, **82**, 1545–50 (1999).

18. S. Hashimoto and A. Yamaguchi, "Synthesis of Needlelike Mullite Particles Using Potassium Sulfate Flux," *J. Eur. Ceram. Soc.*, **20**, 397–402 (2000).

19. H. Wada, K. Sakane, T. Kitamura, and H. Hata, "The Reaction Sequence in the Synthesis of Aluminum Borate Whiskers," *J. Mater. Sci.*, **31**, 537–44 (1996).

20. E. Gonenli and A. C. Tas, "Chemical Preparation of Aluminum Borate Whiskers," *Powder Diff.*, **15**, 104–107 (2000).

21. S. Hayashi, M. Sugai, Z. Nakagawa, T. Takei, K. Kawasaki, T. Katsuyama, Y. Yasumori, and K. Okada, "Preparation of  $CaSiO_3$  Whiskers from Alkali Hydroxide Fluxes," *J. Eur. Ceram. Soc.*, **20**, 1099–103 (2000).

22. Y. Saitou and J. Tanaka, "Crystal Growth of Carbonate Apatite Using  $CaCO_3$  Flux," *J. Mater. Sci., Mater. Med.*, **10**, 561–66 (1999).

23. A. C. Tas, "Production of the Two Inorganic Phases [ $Ca_{10}(PO_4)_6(OH)_2$ ] and [ $Ca_5(PO_4)_3F$ ] Calcium Hydroxyapatite and  $Ca_3(PO_4)_2$ -Tricalcium Phosphate] of Synthetic Bone by Using a Chemical Precipitation Technique," Turk. Pat. No. TR 1995 01421.

24. A. C. Tas, F. Korkusuz, M. Timucin, and N. Akkas, "An Investigation of the Chemical Synthesis and High-Temperature Sintering Behavior of Calcium Hydroxyapatite (HA) and Tricalcium Phosphate (TCP) Bioceramics," *J. Mater. Sci., Mater. Med.*, **8**, 91–96 (1997).

25. B. Mavis and A. C. Tas, "Dip-Coating of Calcium Hydroxyapatite on Ti-6Al-4V Substrates," *J. Am. Ceram. Soc.*, **83**, 989–91 (2000).

26. E. Hayek and H. Newesely, "Pentacalcium Monohydroxyorthophosphate," *Langmuir*, **7**, 63–65 (1993).

27. E. C. Moreno, T. M. Gregory, and W. E. Brown, "Preparation and Solubility of Hydroxyapatite," *J. Res. Natl. Bur. Stand. (U.S.)*, **72A**, 773–82 (1968).

28. M. Jarcho, C. H. Bölen, M. B. Thomas, J. Bobick, J. P. Kay, and R. H. Doremus, "Hydroxyapatite Synthesis and Characterization in Dense Polycrystalline Form," *Mater. Sci. Eng.*, **11**, 2027–35 (1976).

29. D. E. Appleman and H. T. Evans, "Indexing and Least-Squares Refinement of Powder Diffraction Data," U.S. Geol. Survey Rept. No. GI-73-003, 1973.

30. R. Z. LeGeros and J. P. LeGeros, "Dense Hydroxyapatite," pp. 139–80 in *Introduction to Bioceramics*, Edited by L. L. Hench and J. Wilson, World Scientific, Singapore, Republic of Singapore, 1993.

31. N. Kivrik and A. C. Tas, "Synthesis of Calcium Hydroxyapatite-Tricalcium Phosphate (HA-TCP) Composite Bioceramic Powders and Their Sintering Behavior," *J. Am. Ceram. Soc.*, **81**, 2245–52 (1998).

32. A. C. Tas, "Synthesis of Biometric Ca-Hydroxyapatite Powders at 37°C," *Synthetic Body Fluids*, **21**, 1429–38 (2000).