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# Nanostructure processing of calcium phosphates doped with zinc ions

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Calcium phosphates are considered compounds with multiple applications due to biocompatibility and physicochemical properties that it possesses. The purpose of this study is the preparation of calcium phosphates -Zn support for use as a controlled drug delivery system. Nanoscale calcium phosphates was obtained by cold coprecipitation technique and coupling zinc ions occurred in situ. The samples were dried at 100°C and heat treated at 500°C for 2 hours. Powders of calcium phosphates and composites of calcium phosphates and - Zn (1%, 2%, 3% Zn) were characterized by XRD, FT-IR, SEM and EDAX.

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*Keywords:* Nanoscale calcium phosphates, Coprecipitation technique, Calcium phosphates -Zn support

## 1. Introduction

There is a increasing interest for the study of ion substituted calcium phosphate. The apatite structure is very flexible; all the elements can be exchanged if the charge balance is maintained [1]. Hydroxyapatite is a crystalline compound with chemical formula $Ca_{10}(PO_4)_6(OH)_2$ which is part of the apatites group. Hydroxyapatite contains active functional groups that can be replaced by other cations or anions. Recent studies on hydroxyapatite functionalization of copper ions [3], zinc [4], gold [1], silver [5], zinc and silver [6], zinc and copper [7], etc. show that it may be functionalized with a variety of components, with possible applications in the biomedical field. Nanosized calcium phosphates powders could be used as bone repair materials with desired and sustained release of Zn ions [8]. The presence of Zn ions can have effects in stimulation of bone mineralization, protein synthesis and maintaining the structure and function of cell membranes and play an important role in the human immune system [2].

## 2. Experimental

All samples were synthesized with materials of p.a. grade of purity: $(NH_4)_2HPO_4$ (Sigma-Aldrich), $Ca(NO_3)_2 \cdot 4H_2O$ (Sigma-Aldrich), $ZnSO_4 \cdot 7H_2O$ (SC. Silal Trading SRL) and $NH_4OH$ (Sigma-Aldrich). Calcium phosphates without / with doped zinc ion concentrations of 1, 2 and 3% have been prepared by wet method-cold. The solution of 0.5M Ca $(NO_3)_2 \cdot 4H_2O$ was added dropwise to the solution of 0.3M $(NH_4)_2HPO_4$ and homogenized for 24 hours in the presence of 25% $NH_4OH$, to maintain a pH of 9.5. Calcium phosphate doped with zinc ions was prepared following the same steps, but $ZnSO_4 \cdot 7H_2O$ solution was added simultaneously with 3M solution of $Ca(NO_3)_2 \cdot 4H_2O$, in drop. After, this precipitate was washed with bidistilled water four times, then filtered, dried at 100°C /24 h and heat treated at 500°C / 2 h.

Synthesized sample were analyzed by X-ray diffractometry using a SHIMATZU XRD 6000 diffractometer, with CuKα (λ=1.5405 Å) radiation, scanning speed 20/min., in 2θ = 10 - 50 grd range. Fourier transform infrared (FT-IR) spectrofotometry spectra were recorded with Bruker TENSOR 27 spectrometer, over the region of 500-4000 $cm^{-1}$ at a scan rate of 4 $cm^{-1}$, for determine the possible changes in the bonds between the elements of powder obtained. The micrographs (SEM) of powder without/with doped zinc ion are obtained using a Quanta Inspect F scanning microscope and the elemental composition was determined by energy dispersive X-ray spectroscopy (EDAX).

## 3. Results and discussion

The XRD show in Fig.1.It is noted that for powders with 0% and 1% Zn dried at 100$^o$C, the characteristic interferences can be atributed of the monetite ($CaHPO_4$) – $d_1$ = 3.37Ä, $d_2$ = 3.34Ä, $d_3$ = 2.96Ä (ASTM [75-1520]), and the brushite ($CaHPO_4$ $(H_2O)_2$ – $d_1$ = 7.59Ä, $d_2$ = 3.04Ä, $d_3$ = 4.23Ä (ASTM [72-1240]) compounds. Addition of 1% zinc, does not produce changes in the structure of calcium phosphate powder dried at 100 ° C, while the addition of 2 to 3% of zinc change little structure, stabilizing it in calcium hydrogenphosphate (III) hydrate ($Ca(HPO_3)$ $(H_2O)$ – $d_1$ = 7.25Ä, $d_2$ = 2.97Ä, $d_3$ =

3.20Ä (ASTM [71-3060]). After 2 hours of heat treatment at 500°C is observed that the diffraction peaks correspond to hydroxyapatite, $Ca_5(PO_4)_3(OH)$ – $d_1$ = 2.82Ä, $d_2$ = 2.72Ä, $d_3$ = 2.78Ä (ASTM [80-7086]) and the secondary phase, traces of monetite (ASTM [15 -9193]) for powders with 0 and 1% zinc. In the case of powders with 2 and 3% zinc-treated at 500$^o$C, single phase is hydroxyapatite (ASTM [09-0432] – $d_1$ = 2.81Ä, $d_2$ = 2.77Ä, $d_3$ = 2.72Ä. Increasing the sintering temperature to 800°C, the phases mentioned, turns into tricalcium phosphate ($Ca_3(PO_4)_2$ – $d_1$ = 2.88Ä, $d_2$ = 2.60Ä, $d_3$ = 3.20Ä (ASTM [08-8714]) and monetite ($HCa(PO_4)$ – $d_1$ = 3.37Ä, $d_2$ = 3.35Ä, $d_3$ = 2.95Ä (ASTM [09-3755]), regarding of all samples. In 3% zinc powder, in addition, noted the appearance of a compound of zinc, zinc calcium phosphate, $CaZn_2(PO_4)_2$ – $d_1$ = 4.12Ä, $d_2$ = 2.95Ä, $d_3$ = 2.47Ä (ASTM [10-9788]).

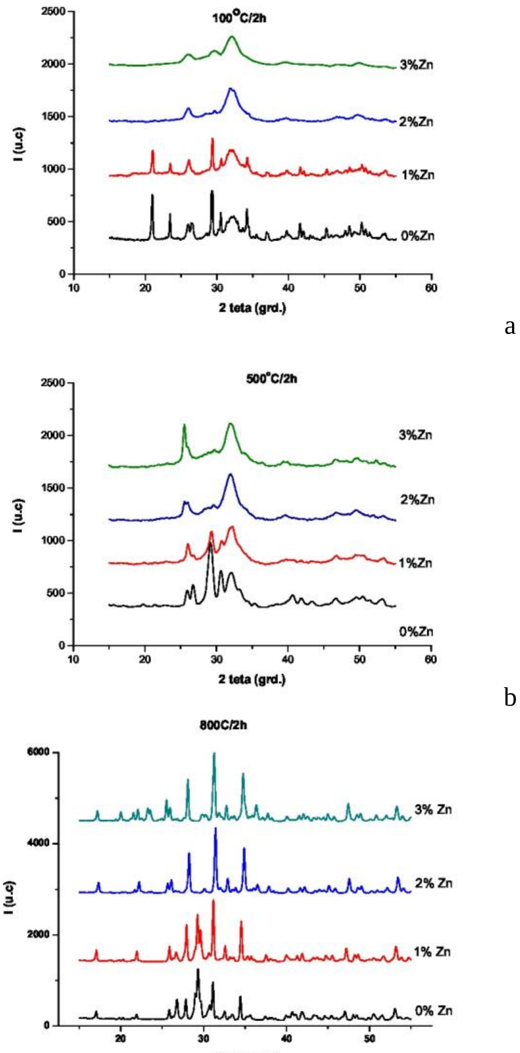


*Fig. 1 Calcium phosphates without / with doped zinc ion powder diffraction patterns, dried at 100$^o$C (a) and annealed at 500$^0$C (b) and 800$^0$C (c)*

FT-IR analyses of calcium phosphates without / with doped zinc ion are shown in Fig. 2. $PO_4^{3-}$ groups forms intensive IR absorption bands in the range of 942 - 1067 $cm^{-1}$, with a maximum at 1030 $cm^{-1}$, due to asymmetric stretching mode of vibration for $PO_4$ group [9]. The -OH bending frequency peaks are observed at 640 $cm^{-1}$ and the -OH streching frequency are observed at 3000 $cm^{-1}$. The presence of two peaks in the region 1384 - 1470 $cm^{-1}$ was due to absorbed carbon dioxide.

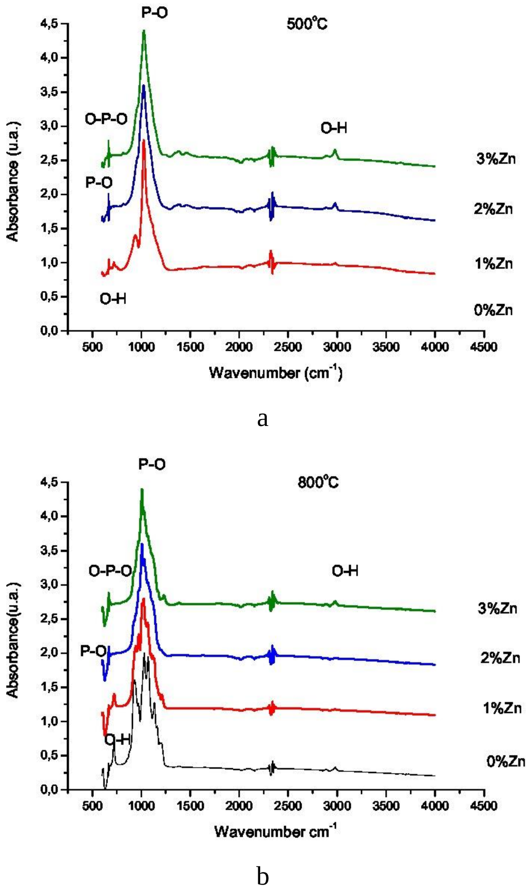


*Fig. 2. FT-IR spectra obtained on samples of calcium phosphate and zinc-doped calcium phosphate (1,2,3% Zn) obtained by cold-precipitation, annealed at 500$^o$C (a) and 800$^o$C (b) /2h*

Scanning microscopy images of samples of calcium phosphate and calcium phosphate doped zinc annealed at 500°C, are shown in Fig. 3. SEM images show agglomerate nanometer particles that, with increasing temperature to 800°C (Fig. 4) is transformed into round shape particles. As shown in the figures below, particle size increases with increasing temperature processing and decreases with increasing percentage of zinc added.

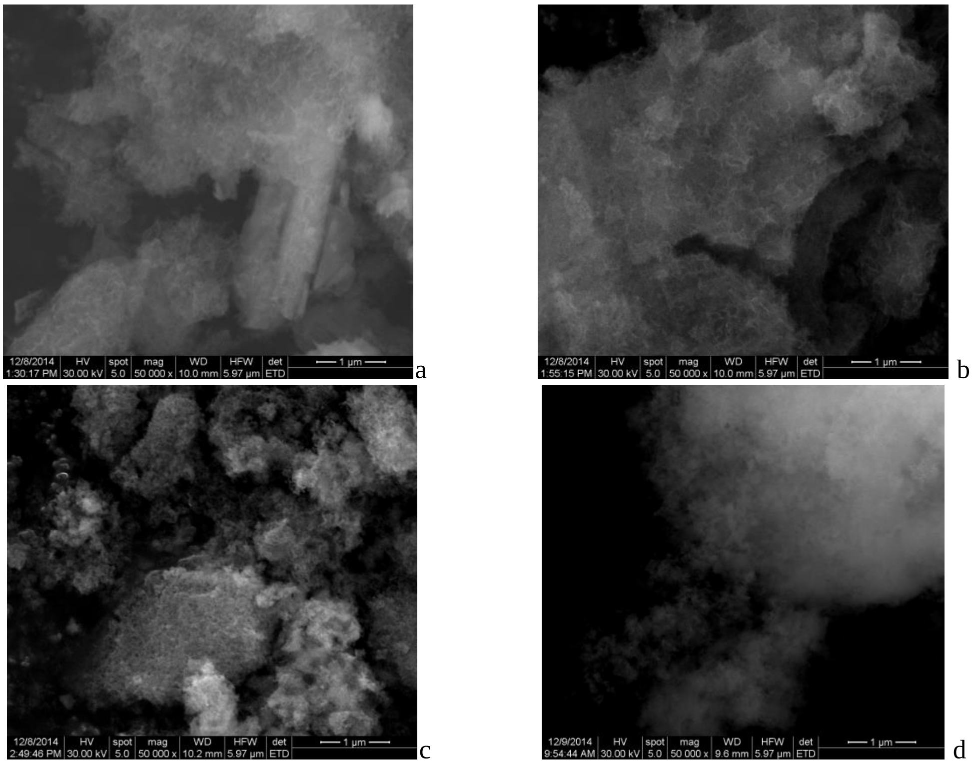


*Fig. 3. SEM images obtained on calcium phosphate (a) and calcium phosphate doped (1,2,3%Zn (b,c,d)), annealed at 500 °C /2h; (a, b, c, d – x 50 000)*

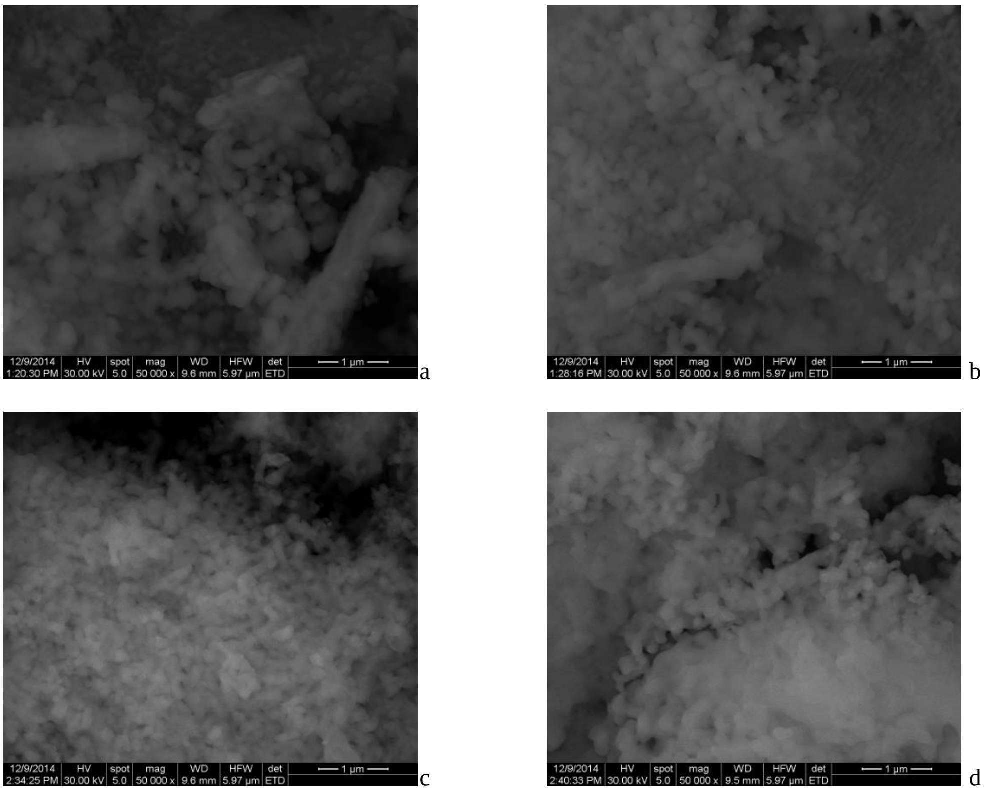
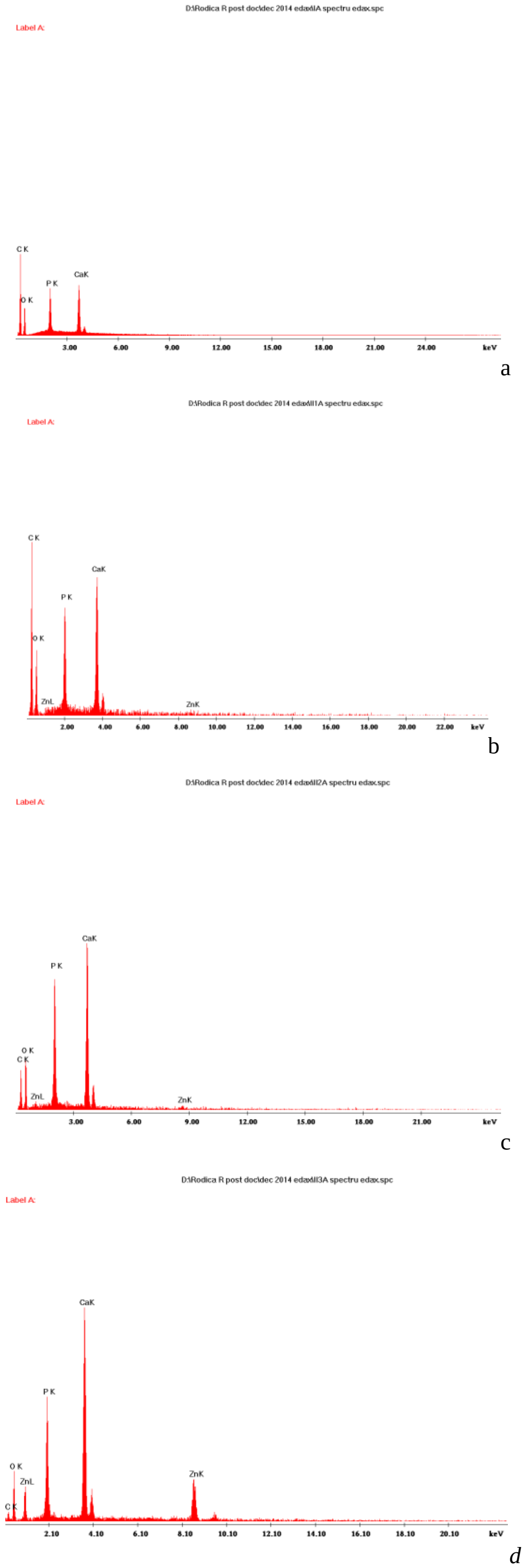


*Fig. 4. SEM images obtained on calcium phosphate (a) and calcium phosphate doped (1,2,3%Zn (b,c,d)), annealed at 800 °C /2h; (a, b, c, d – x 50 000)*



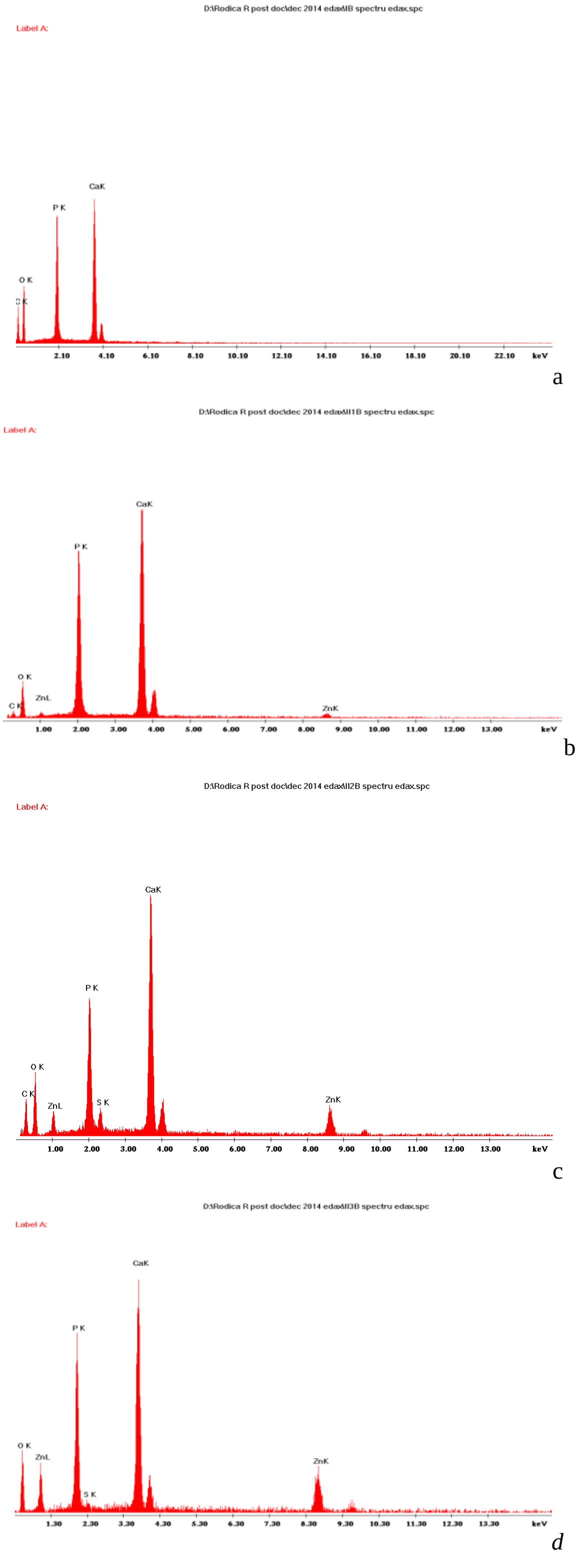
a

b

c

d

*Fig. 5. The X-ray spectra in energy dispersive (EDAX) of the calcium phosphate powders (a) and calcium phosphate doped zinc 1% (b), 2% (c), 3%(d), annealed at 500 $^{o}$C /2h*



a

b

c

d

*Fig 6. The X-ray spectra in energy dispersive (EDAX) of the calcium phosphate powders (a) and calcium phosphate doped zinc 1% (b), 2% (c), 3%(d), annealed at 800 $^{o}$C /2h*

In Fig. 6 are presented EDAX spectra of calcium phosphate samples withoutand composites whith 1,2,3% zinc. Note, the presence of peaks elements Ca, P, O and Zn characteristic of the compound obtained, and carbon, which comes from the grid that was put powder analyzed.

## 4. Conclusion

The presence of zinc durring of calcium phosphates phases influences structural and microcrystaline characteristics; these are in concordance with XRD, FTIR, SEM and EDAX analysis. From point of view of phase composition, the X-ray diffraction analysis shows that at 500°C obtain mixture of phosphate phases- hydroxyapatite with another calcium phosphates phase. Also, at the temperature of 800°C the hydroxyapatite is partial transformed into tricalcium phosphate. At this temperature, in addition, is shown, a crystalline phase of zinc calcium phosphate for the sample doped with 3% zinc.

The microstructural analyses (SEM) shows zinc doping of calcium phosphates influences the dimension of particles, namely, the powders are finer, when the zinc percentage in the sample is higher.

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## References

[1] M. I. Domínguez, F. Romero-Sarria, M. A. Centeno, J.A. Odriozola, Applied Catalysis B: Environmental, **87**(3–4), 245 (2009).

[2] E. P. Domashevskaya, A. A. Al-Zubadi, D. L. Goloshchapov, N. A. Rumyantseva, P. V. Seredin Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques, **8**(6), 1128 (2014)

[3] F. Fernane, M.O. Mecherri, P. Sharrock, M. Fiallo, R. Sipos, Materials Science and Engineering: C **30**(7), 1060 (2010).

[4] F Ren, R Xin, X Ge, Y Leng, Characterization and structural analysis of zinc-substituted hydroxyapatites, Acta biomaterialia, 2009.

[5] Carmen Steluta Ciobanu, Florian Massuyeau, Liliana Violeta Constantin, Daniela Predoi, Structural and physical properties of antibacterial Ag-doped nano-hydroxyapatite synthesized at 100°C, Nanoscale Research Letters, 2011.

[6] Nida Iqbal, Mohammed Rafiq Abdul Kadir, Nasrul Humaimi Mahmood, Norita Salim, Gabriele R.A. Froemming, H.R. Balaji, Tunku Kamarul, Ceramics International, **40(**3), 4507 (2014).

[7] A Tripathi, S Saravanan, S Pattnaik, A Moorthi N C Partridge, N. Selvamurugan, Int J Biol Macromol. **50**(1), 294 (2012).

[8] E. Boanini, M Gazzano, A. Bigi, Ionic substitutions in calcium phosphates synthesized at low temperature, Acta Biomater. 2010.

[9] Liga Berzina-Cimdina and Natalija Borodajenko Research of Calcium Phosphates Using Fourier Transform Infrared Spectroscopy, Infrared Spectroscopy – Materials Science, Engineering and Technology, 2012

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