Canadian Journal of Chemistry
Revue canadienne de chimie

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Journal:	<i>Canadian Journal of Chemistry</i>
Manuscript ID	cjc-2017-0459.R2
Manuscript Type:	Article
Date Submitted by the Author:	13-Mar-2018
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Is the invited manuscript for consideration in a Special Issue?:	N/A
Keyword:	Apatite, lanthanum, barium., DRX

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Preparation and characterization of apatite-like compound

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Abstract

Barium–lanthanum britholite solid solutions, $\text{Ba}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{F}_2$, with $0 \leq x \leq 6$ were prepared by solid state reaction in the temperature range of 1200-1400 °C. The powders were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES), F-selective electrode, X-ray diffraction (XRD) and Fourier transform infra-red (FTIR). In addition, the present study used thermal analysis to follow the apatite formation reaction during the heat treatment. For $x \leq 3$, there is formation of a single apatite phase while above this value, the La_2SiO_5 , $\text{La}_2\text{Si}_2\text{O}_7$, BaSi_2O_5 and $\text{Ba}_2\text{La}_2\text{O}_5$ secondary phases were observed. The variation of the lattice parameters of the apatite phase as a function of x confirmed that the solid solution is discontinuous to either side of $x = 3$.

Keywords: Apatite; lanthanum; barium; DRX.

1. Introduction

The hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAp), the main representative of the apatite's family, has been extensively investigated for various medical applications mainly in orthopedics and dentistry [1-3]. Also, the apatites have attracted more and more attention during the previous

decades due to their thermal and chemical stability, in addition to the various substitutions, that leads to new materials with significant scientific point of view and for technological applications. For example, The substitution of the pair La^{3+} and SiO_4^{4-} for the pair Ca^{2+} and PO_4^{3-} in the fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, Fap) leads to the britholite with the general formula $\text{Ca}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{F}_2$ with $0 \leq x \leq 6$. The compound for $x = 1$ is regarded as a potential matrix for the confinement for the minor actinides and long-lived fission products [4]. On the other hand, the enthalpy of formation of these compounds increases when x rises while it decreases for their counterparts $\text{Ca}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}$ with $0 \leq x \leq 6$ [5]. This family of compounds, especially apatite-type lanthanum silicates, has attracted considerable attention as new class of electrolyte materials for solid oxide fuel cells (SOFCs) [6-10]. They are considered promising candidates to replace yttrium -stabilized zirconia at intermediate temperatures. In addition to these applications, apatites are used in catalysis, [11] chromatography [12-14] or phosphors for fluorescent lamps as [15, 16] or laser materials [17]. As indicated, all these applications are made possible by the various substitutions made in their structure, which confer to the prepared materials a variety of physico-chemical properties, leading to many applications.

Fluorapatite crystallizes mainly in the hexagonal system (space group $P6_3/m$) [18,19]. The PO_4^{3-} groups build the framework and the Ca^{2+} are distributed between two nonequivalent crystallographic sites. Four Ca^{2+} , occupying the S(1), i.e., (4f) sites, are located along the three-fold axis and surrounded by nine oxygen atoms. The six other Ca^{2+} , occupying the S(2), i.e., (6 h) sites, are positioned in the summit of two alternating equilateral triangles centered on a helical six-fold axis of the structure (Fig.1) [20].

In order to enrich the apatite family, the present work describes the attempts to synthesize compounds with the general formula $\text{Ba}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{F}_2$ where $0 \leq x \leq 6$, and define

the solid solution range. This work is part of a systematic study of phosphosilicated apatite containing elements, which result from the fission of uranium-235, such as cesium [21], strontium and barium [22].

2. Experimental

2.1. Powders Preparation

The series of $\text{Ba}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{F}_2$, with $0 \leq x \leq 6$ compounds was synthesized via the high temperature solid-state reaction using barium carbonate ($\text{BaCO}_3 > 99.5\%$ Prolabo), lanthanum oxide ($\text{La}_2\text{O}_3 > 99.9\%$, Aldrich), silica ($\text{SiO}_2 > 99.5\%$ Alfa), ($\text{BaF}_2 > 98\%$ Prolabo) and barium diphosphate ($\text{Ba}_2\text{P}_2\text{O}_7$) according to the following equation:

$\text{Ba}_2\text{P}_2\text{O}_7$ was prepared by heating barium carbonate (BaCO_3) and di-ammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$) (>99% Acros Organics) at 900 °C for 12 h in air, following the equation:

To avoid deviation from stoichiometry, lanthanum oxide was heat-treated at 1000 °C for 2 h just before weighing. Indeed, when La_2O_3 was exposed to air, there was formation of the $\text{La}_2(\text{OH})_{6-2x}(\text{CO}_3)_x$ compound with $x \approx 1$ [23, 24].

Stoichiometric amounts of reactants were carefully ground in an agate mortar during 30 min to ensure their best homogeneity, and then pressed into disks, which were subjected to heat treatments under argon. After a first treatment at 900 °C for 12 h, the samples were treated

again between 1200 and 1400 ° C under flowing argon for 6 h with intermediate re-grinding and re-pelletizing until no reaction is evident by X-ray diffraction.

2.2. Powder characterization

The obtained powders were submitted to a chemical analysis. Barium and lanthanum contents were determined using the Inductive Coupling Plasma Atomic Emission Spectroscopy (ICP-AES) with a Shimadzu ICPQ/V-1014S spectrometer. Si was analyzed by the atomic absorption spectroscopy (Perkin-Elmer 3110) while P content was estimated using the Gee and Deitz method [25], with a Janway 6400 spectrometer. The fluoride (F) concentration was determined by potentiometry using an ionometer equipped with a fluoride specific electrode.

X-ray diffraction (XRD) patterns were recorded on a Philips PW 1800 diffractometer operating in Bragg-Brentano geometry with Cu K α radiation. The samples were scanned in the 2 θ range of 10–60° with a step size of 0.028 and a counting time of 1s per step. The phases in the as-prepared powders were identified by comparing the experimental XRD patterns to the standards compiled by the International Centre for Diffraction Data (ICDD) (N°50–1744). The lattice parameters were determined by the least squares method using AFRAP software [26].

FTIR spectra were recorded from 400 to 4000 cm⁻¹ on a Perkin Elmer Spectrum 100 spectrometer, using the KBr pellet technique.

Thermal analysis was conducted in the air from room temperature to 1300°C at a heating rate of 10°C/min, using a Setaram 92 apparatus.

3. Results and Discussion

3.1. Chemical analysis

The results of the chemical analysis for the synthesized powders are summarized in Table 1. Within the precision of measurements by the different techniques used, there is a satisfactory agreement between the experimental element amounts and those of the used reagents.

3.2. *X-ray diffraction*

XRD patterns showed that all the samples contained an apatitic phase (Figs. 2 and 3). However, two composition ranges can be distinguished. For $x \leq 3$, the patterns exhibited only reflections corresponding to an apatite phase, matching the ICDD card #01-071-1316 for Ba_{10}Fap (Fig. 2), as a single phase. No additional reflections related to the starting reagents or secondary phase, were detected. A shift of the reflections of related to substituted materials to higher angles was observed by increasing the La^{3+} content. This fact could be related to the insertion in the apatite structure.

However, for x values greater than 3, additional reflections related to La_2SiO_5 , $\text{La}_2\text{Si}_2\text{O}_7$, BaSi_2O_5 and $\text{Ba}_2\text{La}_2\text{O}_5$ were detected in addition to those of the apatite (Fig. 3). The intensities of the secondary phases increased with increasing the content of La and Si in the starting mixtures. The formation reactions of the secondary phases, identified on the basis of the ICDD cards, #00-040-0234, #00-048-0052, #00-004-0382 and #00-052-1325, respectively, can be written as follow:

The estimated lattice parameters a and c and the volume are listed in Table 2. The barium fluorapatite parameters are in good agreement with those reported in the literature [20, 27]. However, these parameters decreased gradually with the increase of x value up to a value of 3. A slight variation of these parameters were observed for a substitution values when x value

was greater than 3. The linear evolution of lattice parameters is in agreement with the Vegard's Law [28] as observed in Fig. 4:

$$a = 10.154 - 0.075 x; \quad \sigma(x) = 2.5 \cdot 10^{-3} \text{ \AA}$$

$$c = 7.720 - 0.092 x; \quad \sigma(x) = 1.5 \cdot 10^{-3} \text{ \AA}$$

The decrease of the crystallographic parameters with x could be related to the size of the ions in substitution. However, if Ba^{2+} (coord. 9: $r = 1.47 \text{ \AA}$) was substituted by a smaller ion, La^{3+} (coord. 9: $r = 1.216 \text{ \AA}$) [29], PO_4^{3-} was replaced by a more larger ion, SiO_4^{4-} . Indeed, the Si-O bond lengths ($1.62 \text{ \AA}$) are longer than those of P-O ($1.54 \text{ \AA}$). By synthesizing the series $\text{Sr}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{F}_2$ where $0 \leq x \leq 6$, we observed an inverse trend of the lattice parameters, when the incorporated amounts of La^{3+} and SiO_4^{4-} increased: a increased and c decreased [30]. For this series, Sr^{2+} (coord. 9: $r = 1.31 \text{ \AA}$) was also substituted by a smaller ion, La^{3+} [30] and PO_4^{3-} by SiO_4^{4-} . It is well known that the distribution of the substituent cation between the two non equivalent sites S(1) and S(2) of the apatite structure affects the lattice parameters [20, 31]. Indeed, S(2) sites have a larger effect on the a -axis than on the c -axis, it is the same for the tetrahedrons while the S(1) sites have more influence on c -axis than on the a -axis. Thus, for this latter series, it seems that the size of the silicate group has more effect than that of La^{3+} , on the a -axis. For the nine coordination the difference between the radii of Sr^{2+} et La^{3+} is of $0.10 \text{ \AA}$. Whereas between Ba^{2+} et La^{3+} , this difference is of $0.26 \text{ \AA}$, which explains in the present case the decrease in the a -axis with the increase in the substitution rate, the effect of La^{3+} on this axis becoming preponderant compared to the group of silicates.

The difference in cationic sizes is the widely used effect to explain the formation of the solid solutions. Indeed, studying the substitution of Ba by other divalent cations such as Ca,

Sr and Pb in barium fluorapatite, there is a formation of a continuous solid solution for a difference in the cation size less than 0.15 Å, and a limited solid solution when the difference is higher than this value. [32]. This rule was also verified for other systems [33-35]. In the other hand, other parameters such as electronegativity, coordination number and polarisability have been evoked to have a role on isomorphous substitutions [36].

3.3 Infrared spectroscopy

The FTIR spectra of the as-prepared samples are presented in Fig. 5. The assignments of the absorption bands of the two tetrahedral groups PO_4^{3-} [20, 37] and SiO_4^{4-} [38] were done according to the literature. For $x \leq 3$, the characteristic bands associated to PO_4^{3-} were observed: between 1077-1022 cm^{-1} and at 942 cm^{-1} corresponding to the asymmetric stretching modes (ν_3) and to the symmetric stretching modes (ν_1), respectively. The bands at 544-585 cm^{-1} range were assigned to the asymmetric bending modes (ν_4), while symmetric one (ν_2) was detected at 454 cm^{-1} . The intensities of the reported bands were reduced for x values greater than 1, accompanied with an increase of the corresponding bands related to SiO_4^{4-} groups. These latters were observed at about 915 cm^{-1} (ν_3), 870 (ν_1), between 504 to 543 cm^{-1} (ν_4), and near 420 cm^{-1} (ν_2). When all the phosphate groups were replaced by silicate groups, the spectrum was typical of silicate apatite.

The progressive substitution of the barium ions by lanthanum induced a regular shift of all the adsorption bands towards greater wavenumbers. This might be related to an increase of the anion-anion repulsions in good agreement with the reduction of the lattice dimensions [37]. In the same way, there was decrease of the covalence of the Ba/La–O bonds with the replacement of the barium (Ba^{2+}) ions by lanthanum (La^{3+}) having a polarisability value much smaller than Ba within the apatitic structure. Additional bands related to SiO_2 phase were

observed at 667, 680 and 795, cm^{-1} [39, 40] for x values greater than 4. All the materials exhibited bands at 3600 and 1630 cm^{-1} related to adsorbed molecular water (not shown).

3.4. Thermal behavior

It is well known that the lanthanum oxide (La_2O_3) is very sensitive to moisture and carbon dioxide of air. So, after a prolonged exposure to air, it turns into a mixture of oxide, hydroxide and amorphous hydrated hydroxycarbonate [23, 41-43], according to the following equilibrium reactions:

The TGA/DTA curves of the $\text{Ba}_7\text{La}_3\text{F}_2$ ($\text{Ba}_7\text{La}_3(\text{PO}_4)_3(\text{SiO}_4)_3\text{F}_2$) compound are shown in Fig. 6. The TGA curve exhibit four consecutive mass losses. The first mass loss, observed between 300-400 $^\circ\text{C}$, is related to the dehydration of $\text{La}(\text{OH})_3$ and $\text{La}_2(\text{OH})_4\text{CO}_3 \cdot n\text{H}_2\text{O}$ to LaOOH and $\text{La}_2\text{O}_2\text{CO}_3$, respectively [23, 41-43], and corresponding to a mass loss of 2.31%, following the reported reactions:

The second mass loss step related to the dehydration of LaOOH and occurred at 490 $^\circ\text{C}$, with an weight loss of 1.98%, as followed:

The third and the fourth mass losses were overlapped and occurred in two consecutive steps between 740-950 $^\circ\text{C}$ and 890-950 $^\circ\text{C}$ [23, 41-43] with a mass loss total of 5.29%. These steps were associated to the thermal decomposition of barium carbonate and $\text{La}_2\text{O}_2\text{CO}_3$ compounds as following:

Three structural locations for the carbonate ion have been identified: the first apatite channel, oriented with two oxygen atoms close to the c-axis (type A1); the second close to a sloping face of the PO₄ tetrahedron (type B); and the third stuffed channel position (type A2) [44].

The DTA curve of Ba₇La₃F₂ sample exhibited two endothermic events in the range of 300 - 500 °C. The first was centered at 370 °C due to the dehydration of La(OH)₃ (Eq. 9) and La₂(OH)₄CO₃•nH₂O (Eq. 10). while, the second one was observed at 490 °C, associated to dehydration of LaOOH to La₂O₃ (Eq. 11). There were also three endothermic peak observed at 800, 900 and 912 °C, respectively, which is a result of the thermal decomposition of barium carbonate and La₂O₂CO₃ (Eq. 12 and Eq. 13)) [23, 42, 43, 45].

The total mass loss between 300 °C and 950 °C was about 9.6% for all the samples and it was not affected by the values of x. In the same way, the temperature of DTA events were not affected as well by x values, and indicated that the thermal behavior of the prepared samples was independent of the chemical composition.

Conclusion

Barium phosphosilicate apatites were prepared by a solid state reaction. The obtained powders were characterized by chemical analysis X-ray diffraction, infrared spectroscopy, thermogravimetric and differential thermal analysis. The results indicated that a limited solid solution was formed for a substitution values of x close to 3. Above *this value*, in addition to the apatite phase, La₂SiO₅, La₂Si₂O₇, BaSi₂O₅, and Ba₂La₂O₅ phases were also formed during the preparation of the samples. The incorporation of La³⁺ and SiO₄⁴⁻ ions into the apatite structures induced a decrease of *a* and *c* parameters. This variation was related to the ions size. The infrared absorption spectroscopy confirmed that the substitution of PO₄³⁻ by

SiO_4^{4-} has taken place, and the thermal properties of the apatite were not affected by the incorporation of La^{3+} and SiO_4^{4-} ions at different extents.

References

- [1] Cannizzaro G., Felice P., Leone M., Viola P., Esposito M., Eur. J. Oral Implantol. 2 (2009) 25.
- [2] Stavropoulos A., Karring T., J. Clin. Periodontol. 37 (2010) 200.
- [3] Yukna R.A., Castellon P., Saenz-Nasr A. M., Owens K., Simmons J., Thunthy K. H., Mayer E. T., J. Periodontol. 74 (2003) 679.
- [4] Meis C., Gale J.D., Boyer L., Carpena J., Gosset D., J. Phys. Chem. 104 (2000) 5380.
- [5] Ardhaoui K., Coulet M.V., Ben Chérifa A., Carpena J., Rogez J., Jemal M., Thermochim. Acta, 444 (2006) 190.
- [6] Arikawa H., Nishiguchi H., Ishihara T., Takita Y., Solid State Ionics, 136-137 (2000) 31.
- [7] Nakayama S., Sakamoto M., J. Eur. Ceram. Soc. 18 (1998) 1413.
- [8] Nakayama S., Aono H., Sadaoka Y., Chem. Lett. 6 (1995) 431.
- [9] Schroeder L.W., Mathew M., J. Solid State Chem. 26 (1978) 383.
- [10] Nakayama S., Kageyama T., Aono H., Sadaoka Y., J. Mater. Chem. 5 (1995) 1801.
- [11] Matsumura Y., Sugiyama S., Hayashi H., Moffat J.B., J. Solid State Chem. 114 (1995) 138.
- [12] Schubert S., Freitag R., J. Chromatogr. A 1142 (2007) 106.
- [13] Dattolo L., Keller E.L., Carta G., J. Chromatogr. A 1217 (2010) 7573.
- [14] Benmoussa A., Delaurent C., Lacout J.-L., Loiseau P.-R., Mikou M., J. Chromatogr. A 731 (1996) 153.

- [15] Butler K.H., *Fluorescent Lamp Phosphors, Technology and Theory*, The Pennsylvania State University Press, University Park, PA 1980.
- [16] Welker T., *J. Lumin.* 48-49 (1991) 49.
- [17] DeDoach L.D., Payne S.A., Smith L.K., Kway W.L., Krupke W.F., *J. Opt. Soc. Am. B* 11 (1994) 269.
- [18] Sudarsanan K., Young R.A., *Acta Crystallogr. B* 25 (1969) 1534.
- [19] Elliot J.C., Dykes E., Makie P.E., *Acta Crystallogr. B* 37 (1981) 435.
- [20] Aissa A., Badraoui B., Thouvenot R., Debbabi M., *Eur. J. Inorg. Chem.* (2004). 3828.
- [21] LIDE D.R., *Handbook of Chemistry and Physics*, 73rd edn. (CRC Press, Boca Raton (Florida (USA)), 1992-1993), Section 11.
- [22] Langer A., Stephens W. E., *Phys. Rev.* 58 (1940) 795.
- [23] Panteix P.J., Julien I., Bernache-Assollant D., Abelard P., *J. Mater. Chem. Phys.* 95 (2006) 313.
- [24] Kharlamova T., Pavlova S., Sadykov V., Lapina O., Khabibulin D., Krieger T., Zaikovskii V., Ishchenko A., Salanov A., Muzykantov V., Mezentsseva N., Chaikina M., Uvarov N., Frade J., Argirusis C., *Solid State Ionics* 179 (2008) 1018.
- [25] Gee A., Deitz V. R., *Anal. Chem.* 25 (1953) 1320.
- [26] Lestienne B., Saux M., Vdm R., *AFPAR software*, (1990).
- [27] Aissa A., Badraoui B., Fatteh N., Debbabi M., *J. Soc. chim. Tunisi.* 6 (2004) 203.
- [28] Vegard L., *Zeitschrift für Physik.* 5 (1921) 17.
- [29] Shannon R.D., *Acta Crystallogr. A* 32 (1976) 751.
- [30] Boughzala K., Ben Salem E., Ben Chrifa A., Gaudin E., Bouzouita K., *Mater. Res. Bull.* 42 (2007) 1221.
- [31] Boughzala K., Ben Salem E., Kooli F., Gravereau P., Bouzouita K., *J. Rare Earth* 26 (2008) 483.

- [32] Pauling L., Journal of the American Chemical Society, 51 (1929) 1010.
- [33] Lacout L., Nounah A., Farhat M., Ann. Chim. Sci. Mat. 23(1998) 57.
- [34] Nounah A., Lacout L., J. Solid State Chem. 107(2) (1993) 444.
- [35] Ntathomvukiye I., Kattech I., Jemal M., Ann. Chim. Sci. Mat. 22 (1997) 435.
- [36] Badraoui B., Bigi A., Debbabi M., Gazzano M., Roveri N., Eur. J. Inorg. Chem. 5 (2001) 1261.
- [37] Fowler B.O., Inorg. Chem. 13/1 (1974) 207.
- [38] Khorari S., Cahay R., Rulmon A., Tarte P., Eur. J. Solid State Inorg. Chem. 31 (1994) 921.
- [39] Tzvetkov G., Minkova N., Mater. Lett 39 (1999) 354.
- [40] Hadioui M., Synthèse d'hydroxyapatite et de silices greffées pour l'élimination de métaux toxiques en solution aqueuse, PhD Thesis, University of Toulouse III, France, 2007.
- [41] Béchade E., Julien I., Iwata T., Masson O., Thomas P., Champion E., Fukuda K., J. Eur. Ceram. Soc. 28 (2008) 2717
- [42] Tzvetkov, G., Minkova, N. J. Mater. Sci. Lett. 20 (2001) 1273-1275.
- [43] Bernal S., Botana F.J., Garcia R., Rodriguez-Izquierdo J. M., Thermochim. Acta 66 (1983) 139.
- [44] Fleet M. E., X Liu P. L., Am. Miner., 89 (2004) 1422.
- [45] Tzvetkov G., Minkova N., Solid State Ionics, 116 (1999) 241

Table 1: Chemical analysis (% weight) and experimental composition of $\text{Ba}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{F}_2$ samples

Element\ x	0	1	2	3	4	5	6
Ba	85.990(8)	77.493(7)	69.102(4)	60.479(4)	51.542(6)	43,041(3)	34,208(4)
La		8,701(3)	17.256(2)	26.056(2)	35.101(5)	43,791(3)	52,821(5)
P	11.629(7)	9,712(2)	7.753(4)	5.809(7)	3.933(4)	1,925(4)	-
Si		1,721(6)	3.541(2)	5.321(4)	7.027(5)	8,838(5)	10,609(3)
F	2.381(5)	2,368(2)	2.348(2)	2.335(3)	2.388(5)	2,398(4)	2,360(2)
Experimental formula							
X=0	$\text{Ba}_{9.99}(\text{PO}_4)_{5.99}\text{F}_2$						
X= 1	$\text{Ba}_{9.01}\text{La}_1(\text{PO}_4)_{3.99}(\text{SiO}_4)_{0.98}\text{F}_{1.99}$						
X=2	$\text{Ba}_{8.02}\text{La}_{1.98}(\text{PO}_4)_{6-x}(\text{SiO}_4)_{2.01}\text{F}_{1.97}$						

Table 2: Lattice parameters of $\text{Ba}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{F}_2$ samples

Sample	a (Å)	c (Å)	V (Å ³)
$x = 0$	10.157(3)	7.732(4)	690.801(4)
$x = 1$	10.075(4)	7.612(6)	669.143(9)
$x = 2$	10.001(1)	7.531(3)	652.334(6)
$x = 3$	9.9310(2)	7.451(5)	636.401(2)
$x = 4$	9.911(5)	7.434(2)	632.394(4)
$x = 5$	9.901(3)	7.422(1)	630.100(3)
$x = 6$	9.891(6)	7.410(4)	627.811(7)

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Figures captions

Figure 1: Perspective view of the fluoroapatite structure

Figure 2: Powder XRD patterns of $\text{Ba}_{10-x}\text{La}_x(\text{PO}_4)_6(\text{SiO}_4)_x\text{F}_2$ samples with $x = 0, 1, 2$ and 3 compositions.

Figure 3: Powder XRD patterns of $\text{Ba}_{10-x}\text{La}_x(\text{PO}_4)_6(\text{SiO}_4)_x\text{F}_2$ samples with $x = 4, 5$ and 6 compositions.

Figure 4: Variation of the a and c parameters of the $\text{Ba}_{10-x}\text{La}_x(\text{PO}_4)_6(\text{SiO}_4)_x\text{F}_2$ samples in function of chemical composition " x "

Figure. 5: FTIR spectra of $\text{Ba}_{10-x}\text{La}_x(\text{PO}_4)_6(\text{SiO}_4)_x\text{F}_2$ materials with different compositions.

Figure.6: Thermogravimetric and differential thermal analysis (TGA-DTA) features of $\text{Ba}_7\text{La}_3(\text{PO}_4)_3(\text{SiO}_4)_3\text{F}_2$ sample.

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Figure 1

Figure 2

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