

# **Immobilization of Cs/Sr fraction of radioactive wastes into phosphorus and silicon containing compounds of pollucite structure**

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# 1. Introduction

## 1.1 High Level Waste

A nuclear power plant of 1 GW(e) produces on average 20 metric tons of spent fuel annually (Feiveson et al., 2011). This spent fuel can be disposed directly (open fuel cycle) or it can be reprocessed to extract the uranium and plutonium and reduce the total volume of the waste (IAEA, 2008; Arthur et al., 1973; Taebi et al., 2008). During spent nuclear fuel reprocessing, for example PUREX and other modifications of PUREX, three types of wastes are produced, namely Low Level, Intermediate level and High Level Waste.

A typical 1 GW(e) nuclear power station generates about 1 ton of fission products and minor actinides per year (Lennemann, 2011; IAEA, 2012). This high level waste (HLW) contains more than 95% of the total radioactivity produced in the nuclear power generation. The majority of radio toxicity in HLW is produced by minor actinides which increase the total storage time of the waste (figure 1).

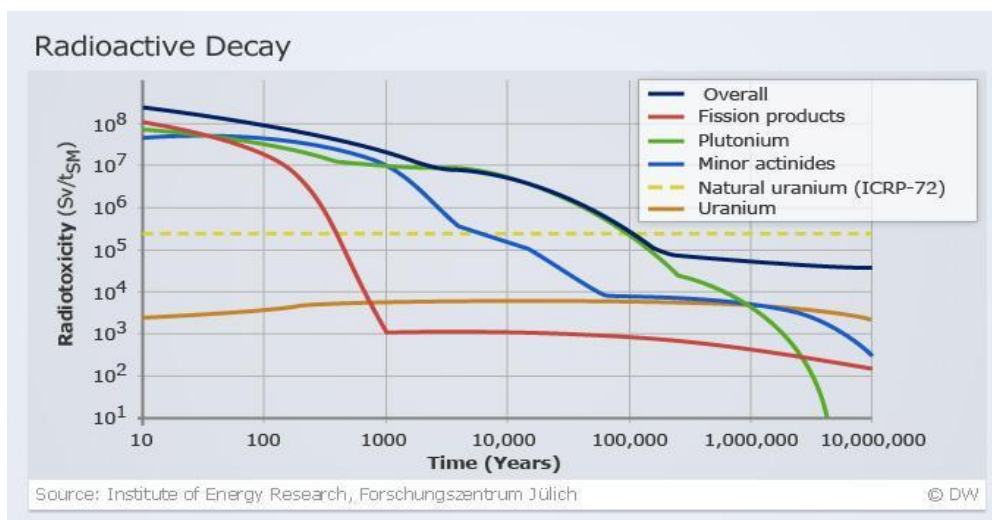


Figure 1 Radio toxicity of FP, MA, Pu, U over time compared to the natural uranium ore

One of the approaches to manage HLW is to separate the waste into several groups to optimize final disposal (IAEA, 2008; Arthur et al., 1973). Studies suggest to separate the minor actinides for transmutation to reduce their radio toxicity and required storage time (Warin, 2011).

The total package density of the waste packages of HLW that has to be disposed of underground is temperature limited by the repository requirements (<100 °C). By

removing the heat generating fission products, the volume of the total waste will be significantly reduced (*Law et al., 2006*). This means that more loading in HLW is possible before reaching 100 °C in the waste package (*Verhoef et al., 2011*).

## 1.2 Cesium and strontium

Radioactive isotopes Cs-137 and Sr-90 are the two most heat generating fission products present in HLW. Cs-137 and Sr-90 have a specific power of  $0.097 \text{ Wg}^{-1}$  and  $0.142 \text{ Wg}^{-1}$  respectively. Cs-137 has a half live of 30 years and Str-90 a half live of 28.8 years (*HyperPhysics Nuclear, 2011*). Both emit beta radiation. In the decay process of Cs-137, also gamma rays are emitted. Cesium and strontium also mimic the chemical properties of respectively potassium and calcium, which are crucial for all organisms. When ingested, they can potentially cause cancer and damage tissue (*HyperPhysics Nuclear, 2011; Apalin et al., 1965*). This may happen when these radionuclides are uptaken in the food chain trough soil and groundwater. In (*Sims et al., 2008*) the mobility of cesium and strontium has been studied for prairie soil , collected at the site of 1951 leak from an aqueous solution of irradiated uranium. In this study diffusion coefficients between  $0.6 \cdot 10^{-4}$  and  $3.0 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1}$  for Cs-137 and  $1.6 \cdot 10^{-9}$  and  $2.6 \cdot 10^{-9}$  for Sr-90 were measured. Cesium and strontium can be immobilized simultaneously as a single waste form that has to be stored above ground. This requires co-extraction of cesium and strontium (*Bohre et al., 2013; Clarke, 1983; Mingfen et al., 2012*).

## 1.3 Co-extraction of cesium and strontium

(*Law et al., 2006; Todd T.A., 2004; Todd T.A., 2005*)

Simultaneous extraction reduces overall complexity of reprocessing and reduces the total space, facilities, as well as chemical reagents. Several schemes have been developed and demonstrated to separate Cs and Sr simultaneously from dissolved spent fuel. Solvent extraction is the most applicable and promising technology for acidic HLW (*Law et al., 2006; Xu et al., 2012*). Two solvent extraction technologies are being developed: CCD/PEG and FPEX.

The CCD/PEG process uses the extractants chlorinated cobalt dicarbollide/polyethylene glycol (CCD/PEG) which can be used to extract cesium with CCD and strontium with PEG.

The FPEX process is based on a combined solvent containing two extractants: 4,4',(5')-Di-(t-butylidicyclo-hexano)-18-crown-6 (DtBuCH18C6) for Sr and Calix[4]arene-bis-(tertoctylbenzo-crown-6) (BOBCalixC6) for Cs.

Both processes have been tested with simulated feed and only CCD/PEG has also been tested with actual LWR feed. From (*Law et al., 2006*) experimental data of the CCD/PEG process have been used to calculate the Cs/Sr fraction in the product stream (table 1).

**Table 1 Feed and product stream compositions for Cs and Sr after CCD/PEG**

	Feed ( $10^{-3}$ mole L <sup>-1</sup> )	Removal efficiency CCD/PEG	Product stream ( $10^{-3}$ mole L <sup>-1</sup> )
Cesium	2.33	99.6%	2.32
Strontium	1.60	99.9%	1.60

The product stream consists of 59.2 mole% of cesium and 40.8 mole% of strontium. These percentages are dependent on the removal efficiencies and the initial feed compositions.

## 1.4 Isolation and solidification of Cs/Sr waste form

The safe isolation of the separated Cs/Sr fraction from the biosphere requires immobilization of the radionuclides in a solid matrix for they have to be disposed for at least three hundred years to decay to a stable isotope (*Bohre et al., 2013*). The waste form should possess a chemical, physical, thermal and radiation stability and resist leaching, powdering, cracking, and other modes of degradation and have a good heat conduction. The waste matrix should also be relatively inexpensive for fabrication and easy to handle.

The current technology for disposing HLW is mainly solidification of the entire HLW content in a glass matrix. The disadvantages of this method are thermal instability and devitrification (*Mingfen et al., 2012; Montel, 2011; Ojovan et al., 2007*). In France and UK borosilicate glass is used. This type of glass should be handled below 700 °C. In Russia phosphate glass is applied, which has to be handled below 400 °C.

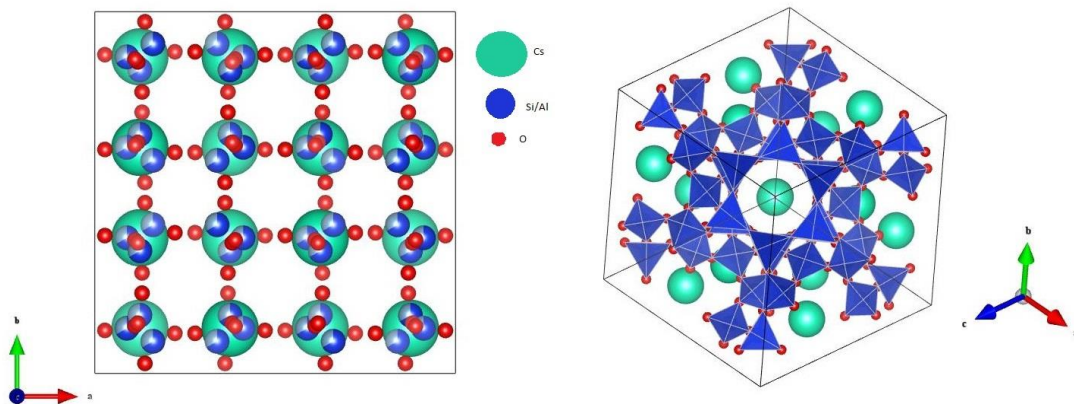
In general, ceramic materials based on the structure of natural minerals draw attention as an alternative to glass, because they excel glass with respect to chemical, thermal and radiation stability (*Clarke, 1983; Montel, 2011; Mingfen et al., 2012; E*). Ceramic waste

forms know three principle classes of oxide ceramics: alumina-based ( $X(\text{Al,Fe})_{12}\text{O}_{19}$  with  $X=\text{Sr, Ba}$ ), titanate-based ( $\text{Zr}(\text{Ca, Mn})_2(\text{Fe, Al})_4(\text{Ti}_3\text{O}_{16})$ ) and silicate-based. A natural occurring mineral with Cs in the matrix is pollucite,  $\text{CsAlSi}_2\text{O}_6$ . Phosphates are also of great interest, for example structure types of monazite and kosnarite.

## 1.5 Pollucite as a host for radioactive waste

Several studies have shown that pollucite is a promising host to immobilize cesium (*Komarneni et al., 1981; Yanagisawa et al., 1984; Yanagisawa et al., 1986; Loginova et al., 2011; Hirst et al., 2003*).

Pollucite is a natural occurring mineral with a chemical formula  $(\text{Cs,Na})\text{AlSi}_2\text{O}_6 \cdot x\text{H}_2\text{O}$ . Its structure was first investigated by Náráy-Szabó in 1938 (*Naray-Szabo, 1938; Beger, 1969*). Cesium is naturally hosted by the pollucite in  $\text{Cs}[\text{AlSi}_2\text{O}_6]$  in large twelve-coordinates voids.  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  are randomly distributed over the tetrahedral sites and the total charge is balanced by oxygen. The space group of this mineral is cubic  $Ia\bar{3}d$  with cell parameter  $a = 13.69 \text{ \AA}$  (*Beger, 1969; Hirst et al., 2003*). The structure of  $\text{Cs}[\text{AlSi}_2\text{O}_6]$  and the mineral are shown in figure 2 and 3 respectively.



**Figure 2** The structure of  $\text{Cs}[\text{AlSi}_2\text{O}_6]$ , where cesium is the void cation and Si, Al and O are the interstitial ions



**Figure 3** A sample of pollucite ore

Pollucite belongs to the structural family of analcime with a general crystal chemical formula  $T_{16}M_{24}[(T',T'')_{48}O_{96}]$ , where T stands for the large void cations, M for the medium-sized void cations, occupying one position and T' and T'' are tetrahedrally coordinated interstitial cations, totally occupying three positions. The framework of the structure of pollucite minerals is based on tetrahedral (Si, Al)O<sub>4</sub> bonds with six oxygen (Loginova et al., 2011; Beger, 1969).

Isomorphism is the phenomenon of the occurrence of a group of minerals that have the same crystal structure (iso-structural) and in which specific sites can be occupied by two or more elements, ions, or radicals. The term therefore requires the substitution of one or more elements for another element (or elements) in the mineral structure. This process or phenomenon is also known as “solid solution”.

The Goldschmidt’s rule states, if the radii difference between the two cations is less or equal to 15%, isomorphism is extensive (West, 1984). There are exceptions to this rule, for example for the NZP structure types (isomorphism between Cs[Zr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>] and Sr[FeZr(PO<sub>4</sub>)<sub>3</sub>]). The radii difference between Cs and Sr is about 30%.

In heterovalent isomorphism the charge is important. Substitution of cations with a lower or higher charge can lead to vacancies in the structure (West, 1984).

Loginova et al., 2011 have studied isomorphous compounds with phosphorous-containing frameworks crystallized in pollucite structure and have calculated the possible formula compositions of compounds with the expected pollucite structure  $T[T'_{3-x}P_xO_6]$ , T and T' are void and framework cations respectively: x=1 , 1.5. A, B, R and M are cations in oxidation states 1+, 2+, 3+ and 4+, respectively (table 2).

**Table 2 Theoretically possible formula compositions of phosphorous-containing compounds with the expected pollucite structure**

Framework charge	Void cations T	Framework cations T'	
		x=1	x=1.5
1	A	MB $M_{4/3}A_{2/3}$ RR	$M_{5/4}B_{1/4}$ $R_{1/2}B$ $RA_{1/2}$
1.5	$M_{1/6}A_{5/6}$ $R_{1/4}A_{3/4}$ $B_{1/2}A_{1/2}$	$M_{1/4}R_{7/4}$ $M_{3/4}B_{5/4}$	$R_{3/4}A_{3/4}$ $M_{1/2}A$
2	$M_{1/3}A_{2/3}$ $R_{1/2}A_{1/2}$ B	MA RB $M_{1/2}B_{3/2}$ $R_{3/2}A_{1/2}$	$M_{1/3}A_{7/6}$ $R_{1/2}A$ $BA_{1/2}$

It should be noted that phosphorus-containing pollucites are a relatively new family of materials. Besides, phosphorus is already available in the HLW originating from tri-butyl phosphate (TBP) from the PUREX process, which is ideal for a “waste into waste” prospect. In general silicon based compounds tend to form polymers easily and are tricky to synthesize. The space group of the phosphorous containing compounds decreases relative to the natural pollucite mineral from Ia3d to I4<sub>1</sub>32 (Hirst *et al.*, 2003; Loginova *et al.*, 2011).

Different methods have been used to synthesize pollucite, for example hydrothermal hot-pressing and sol-gel, and the product was characterized by X-ray powder diffraction (Gallagher *et al.*, 1981). Solid solutions of pollucite structure were also examined with other interstitial cations, for example Cs[FeSi<sub>2</sub>O<sub>6</sub>], Cs[BSi<sub>2</sub>O<sub>6</sub>], Cs[Al<sub>2</sub>PO<sub>6</sub>], Cs[AlLi<sub>0.5</sub>P<sub>1.5</sub>O<sub>6</sub>] and Cs[MgAl<sub>0.5</sub>P<sub>1.5</sub>O<sub>6</sub>], based on the principles of isomorphism (Mazza *et al.*, 1996; Loginova *et al.*, 2011). In (Aloy *et al.*, 2000) Cs[AlLi<sub>0.5</sub>P<sub>1.5</sub>O<sub>6</sub>], a new pollucite-type compound, has been formed as a precipitate on top of cesium aluminophosphate glass.

Natural pollucite has a leaching rate of approximately  $2.2 \cdot 10^{-6} \text{ g cm}^{-2} \text{ day}^{-1}$ , while Cs[MgAl<sub>0.5</sub>P<sub>1.5</sub>O<sub>6</sub>] has a leaching rate of around  $7.1 \cdot 10^{-6} \text{ g cm}^{-2} \text{ day}^{-1}$ . When borosilicate glass is leached, altered surface layers are formed. The highest cesium leaching rate for this type of glass is  $1.25 \cdot 10^{-3} \text{ g cm}^{-2} \text{ day}^{-1}$  (Aloy *et al.*, 2012). All leaching rates mentioned above have been determined in demineralized water for approximately 30 days at room temperature.



Natural pollucite has a melting point of above 1900 °C, however around 1650 °C cesium loss from the pollucite matrix occurs. The maximum thermal stable temperature for pollucite is around 1500 °C, while for borosilicate glass it is 700 °C (*MacLaren et al., 1999*).

Investigations by differential thermal analysis (DTA), differential thermogravimetric analysis (DTG) and IR spectrometry have been done. Also the cell parameters, thermal expansion and phase stability have been determined (*Gatta et al., 2009; Clarke, 1983; Gallagher et al., 1981; Yanagisawa et al., 1986; Loginova et al., 2011*).

The aim of this project was to test the pollucite structure for simultaneous inclusion of Cs and Sr. Silicon and phosphorus based compounds were synthesized by different methods, namely sol-gel, solid state and Pechini. Different techniques were applied for investigation and characterization, such as gravimetric analysis, ICP-OES, XRD and SEM-EDS.

## 2. Experimental

### 2.1 Synthesis

In this work three different procedures were used for the synthesis of Cs and Sr containing pollucites: namely the sol-gel, the solid-state and the Pechini method.

In the sol-gel method the starting materials, which are metal nitrates and colloidal inorganic solutions, are added in stoichiometric amounts together forming an integrated network (gel) of polymers. This gel is mixed to form a homogeneous solution. The excess of liquid is removed by a drying process. In this study not always a precipitation or polymer was formed.

In the solid-state method the starting materials are in powder form when stoichiometrically mixed together (eventually with isopropanol) for homogenization. Here no necessary drying process is required.

The Pechini method requires dissolving metal nitrates in organic solutions, namely citric acid,  $C_6H_8O_7$  and ethylene glycol,  $C_2H_6O_2$ , in stoichiometric ratios. Citric acid is a chelating agent, forming metal complexes (metallic citrate). The metal complexes are then esterified with ethylene glycol forming an organic gel with a homogeneous distribution of the metals (*Lee et al., 2003; Barre et al., 2005*) (figure 4).

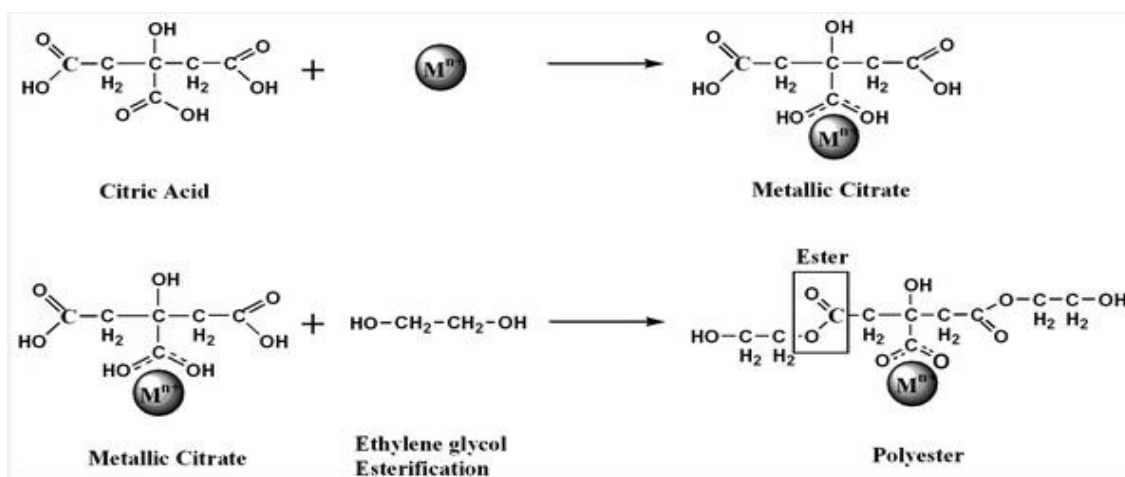


Figure 4 Scheme of Pechini method reactions

For both methods nitrates of cesium,  $Cs(NO_3)$  (Alfa Aesar, 99.9%) and strontium,  $Sr(NO_3)_2$  (Sigma-Aldrich, >99%) were used.

For the sol-gel method phosphorous acid,  $H_3PO_4$  (1.41 M) and a colloidal dispersion of 30% silicon(IV)oxide,  $SiO_2$ , in ethylene glycol were used. Nitrate solutions of iron,  $Fe(NO_3)_3$  (0.51 M), magnesium,  $Mg(NO_3)_2$  (1.04 M) and lithium,  $Li(NO_3)$  (0.50 M) were first prepared and then analyzed with ICP-OES.

For the solid-state method diammonium monohydrogen phosphate,  $(NH_4)_2HPO_4$ , silicon(IV)oxide (amorphous),  $SiO_2$ , nitrates of nickel,  $Ni(NO_3)_2$  and iron,  $Fe(NO_3)_3$ , lithium carbonate,  $Li_2CO_3$ , titanium(IV)oxide,  $TiO_2$  and boric acid,  $H_3BO_3$  were used.

After mixing and drying the samples underwent a heat treatment for denitration and decarbonation at 600 °C for 12 hours. At this temperature the powder is not yet crystallized. Therefore the samples underwent another heat treatment to crystallize at 800 °C for 24 hours. Some samples were heated up till 1000 °C for 4 hours. The temperatures and duration of heat treatments were chosen based on different studies as in *Gallagher et al., 1981; Gatta et al., 2009; Clarke, 1983; Gallagher et al., 1981; Yanagisawa et al., 1986 and Mazza et al., 1996.*

Between the heating steps grinding of the samples were required to achieve homogenization. This was done with a agate mortar and a vibration mill.

In figure 5 and 6 the schematic representations of respectively sol-gel and Pechini methods are shown.

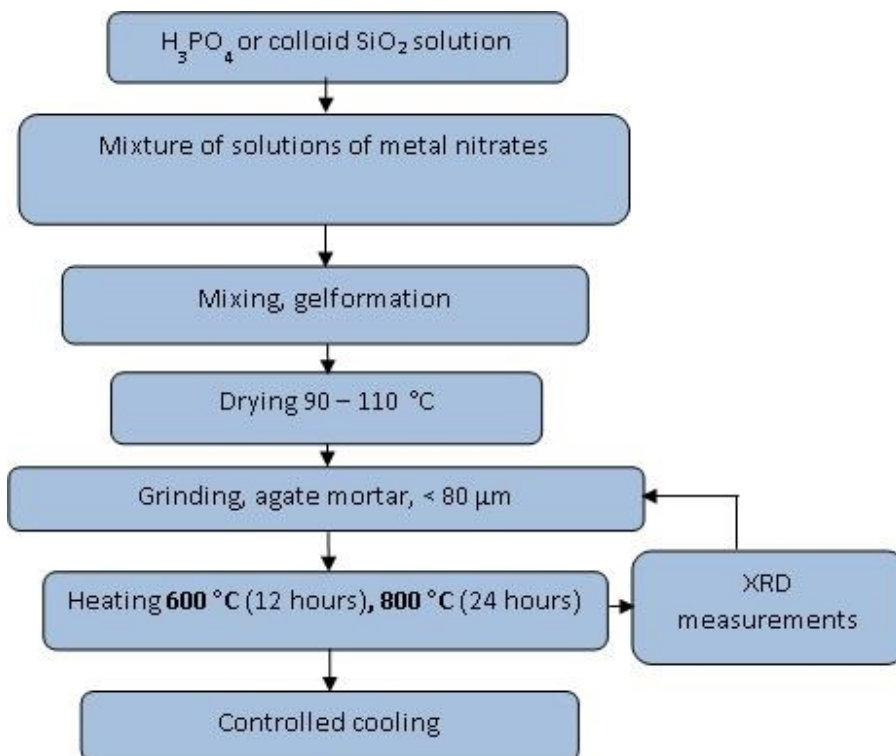


Figure 5 A schematic representation of the sol-gel method

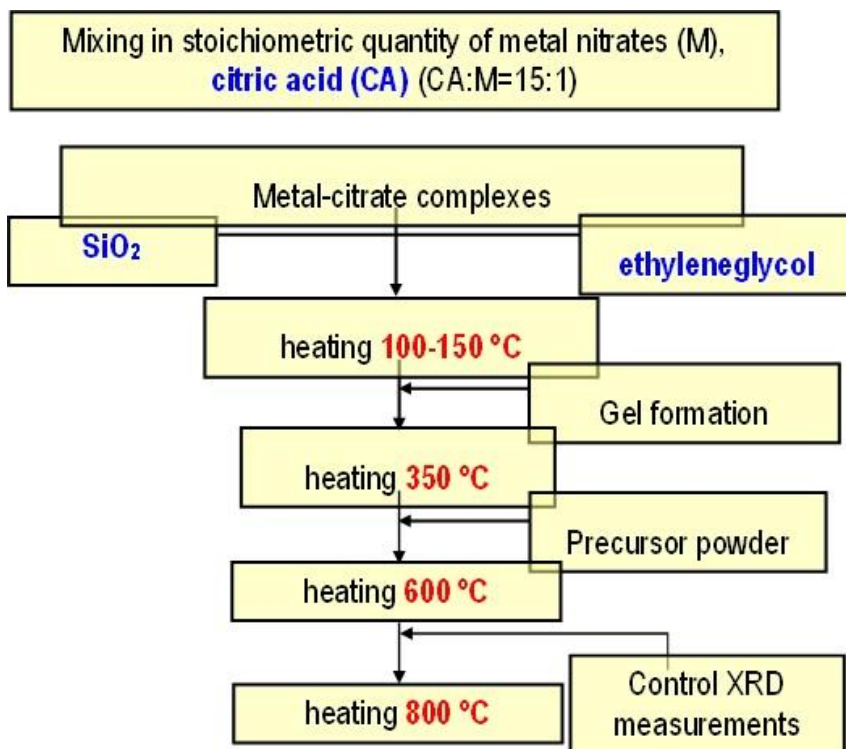


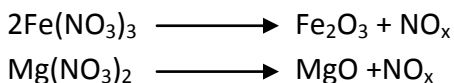
Figure 6 A schematic representation of the Pechini method

## 2.2 Investigation Methods

The solutions of iron nitrate and magnesium nitrate were made of crystal hydrates:  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , respectively. Before the solutions could be used for synthesis their actual concentration had been determined. This was done by gravimetric analysis and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

### Gravimetric analysis

The iron and magnesium nitrate solutions, known volume, were dried and decomposed at high temperature to their oxides which were weighed. The concentration of the nitrate solution could be calculated using the conservation of mass law.



### ICP analysis

The nitrate solutions were diluted to different concentrations within the calibration curve. The ICP analysis used a standard with known concentration to determine the actual concentration of the solutions.

The ICP analysis is based on the Beer-Lambert Law:

$$A = \epsilon bC$$

A = the measured absorbance (arbitrary units)

$\epsilon$  = a constant and is determined from a Beer-Lambert plot (absorbance vs. conc.)  
(L mole<sup>-1</sup> cm<sup>-1</sup>)

b = the path length of the sample cell (cm) and

C = the concentration of the sample (mole L<sup>-1</sup>)

### XRD analysis

The phase analysis of the compounds was done by X-ray diffraction. X-ray diffraction patterns are specific for every powder. The diffraction patterns were obtained at 45 kV, 40 mA in the 2 $\theta$  range of 10° - 50°,  $\lambda(\text{CuK}\alpha) = 1.54046 \text{ \AA}$ . The obtained diffractogrammes were compared to standard patterns which are collected in the Powder Diffraction File. The cell parameters were calculated by the programme Fullprof(Rodriguez-Carvajal, 1993) and the structures were analyzed by Vesta (Momma, 2013).

### SEM-EDS

A microscopic analysis was done by Scanning Electron Microscopy (SEM) and a semi-quantitative by Energy Dispersed Spectroscopy (EDS) detection. A primary electron beam enters the surface of the sample which leads to generation of secondary, backscattered electrons and X-rays. Images are obtained by the secondary electrons. The intensity of the backscattered electrons correlate to the atomic number of the element and the X-rays can give quantitative information about the composition of the sample. Li could not be detected with this analysis because its K X-rays are of too low energy to be detected by EDS. For real accurate data, a flat, homogeneous and polished surface is required (ammrf, 2012).

### 3. Results and Discussion

According to table 1,  $\text{Cs}[\text{Fe}_{0.5}\text{MgP}_{1.5}\text{O}_6]$  and  $\text{Cs}[\text{Li}_{0.5}\text{FeP}_{1.5}\text{O}_6]$  have a framework charge of 1 for  $x=1.5$ , with the theoretically possible formulas of  $\text{AR}_{1/2}\text{B}$  and  $\text{ARA}_{1/2}$  respectively. These compositions has been chosen as a starting material.

If strontium was gradually inserted in the matrix, the following series of chemical compositions could be expected:  $\text{Cs}_x\text{Sr}_{(1-x)} [\text{Fe}_{(1-0.5x)}\text{MgP}_{(1+0.5x)}\text{O}_6]$  and  $\text{Cs}_x\text{Sr}_{(1-x)} [\text{Fe}_{(0.5+0.5x)}\text{Li}_{(1-0.5x)}\text{P}_{1.5}\text{O}_6]$ .

Both composition series have been synthesized for  $x=0, 0.2, 0.4, 0.6, 0.8$  and  $1$ .

The phase analysis diffractogrammes of the compounds with chemical formulas of  $\text{Cs}_x\text{Sr}_{(1-x)} [\text{Fe}_{(1-0.5x)}\text{MgP}_{(1+0.5x)}\text{O}_6]$  after  $800^\circ\text{C}$  for  $x=0, 0.2, 0.4, 0.6, 0.8$  are given in figure 7. These compounds were synthesized with the sol-gel method.

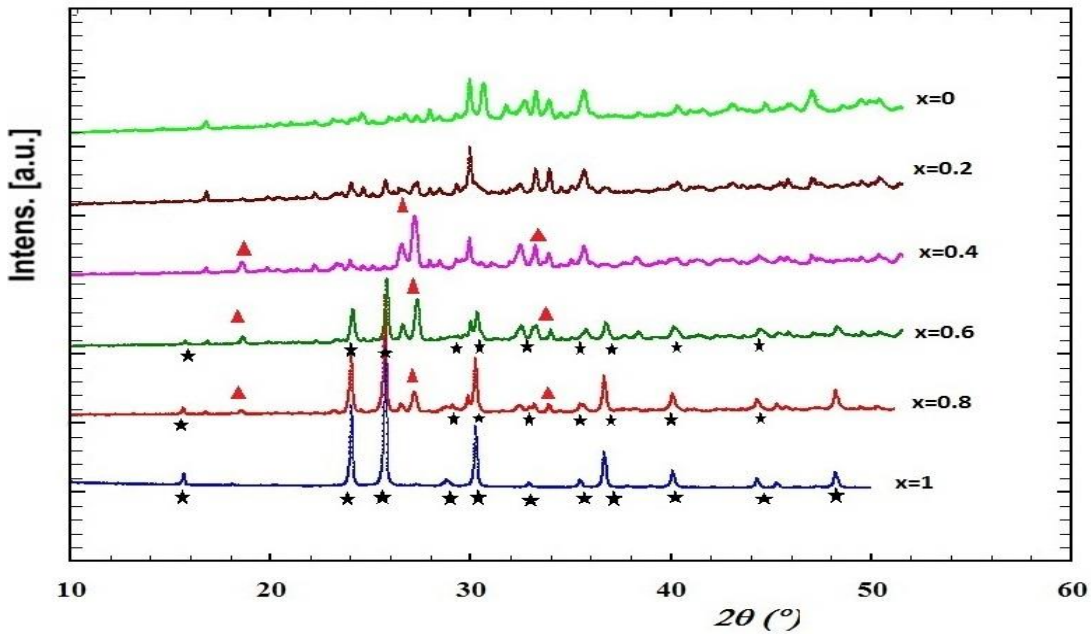


Figure 7 XRD data for  $\text{Cs}_x\text{Sr}_{(1-x)} [\text{Fe}_{(1-0.5x)}\text{MgP}_{(1+0.5x)}\text{O}_6]$ , after  $800^\circ\text{C}$ ,  $x=0, 0.2, 0.4, 0.6, 0.8, 1$ , with  $\blacktriangle = \text{CsMgPO}_4$ ,  $\star = \text{pollucite Cs}[\text{Fe}_{0.5}\text{MgP}_{1.5}\text{O}_6]$

The diffractogram for  $x=1$  shows the diffraction pattern of pollucite  $\text{Cs}[\text{Fe}_{0.5}\text{MgP}_{1.5}\text{O}_6]$ . The stars indicate the peaks which are specific for pollucite, the main phase. However some peaks from minor quantities of  $\text{MgO}$  and  $\text{Mg}_3(\text{PO}_4)_2$  were also detected.

When cesium is replaced by strontium for 20% ( $x=0.8$ ) the diffractogram indicates that the main phase still has a pollucite structure, while the red triangles indicate that

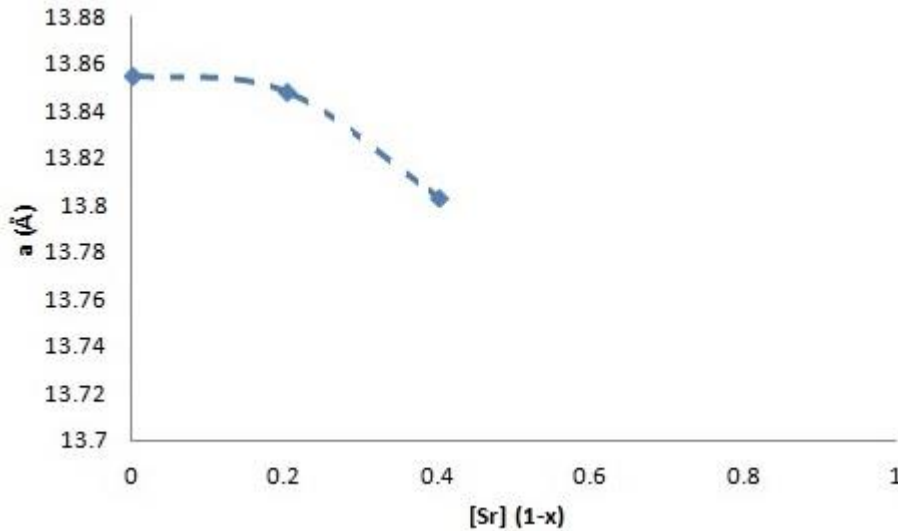
another phases with a composition of  $\text{CsMgPO}_4$  and the orthorhombic strontium pyrophosphate ( $\text{Sr}_2\text{P}_2\text{O}_7$ ) was formed. The amount of these phases increase as the amount of strontium is increased.

At 40% of strontium in the void ( $x=0.6$ ) pollucite is just a minor phase.

For  $x=0.4, 0.2$  and  $0$  the result was a mixture of simple oxides and phosphates, for example  $\text{Fe}_2\text{O}_3, \text{SrO}, \text{MgO}, \text{Mg}_3(\text{PO}_4)_2$  and  $\text{CsMgPO}_4$ .

To make sure that the pollucite phase consisted of strontium in the void and not only  $\text{Cs}[\text{Fe}_{0.5}\text{MgP}_{1.5}\text{O}_6]$ , the cell parameters of the compounds up to 40% of strontium were analyzed.

In figure 8 the cell parameters versus the amount of strontium in the matrix are shown.



**Figure 8** The cell parameters as a function of the Sr concentration for  $\text{Cs}_x\text{Sr}_{(1-x)}[\text{Fe}_{(1-0.5x)}\text{MgP}_{(1+0.5x)}\text{O}_6]$

This data shows that for  $x=0.6 - 1$  the inclusion of smaller Sr leads to the decrease of the cell parameter. The radii of  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  are respectively  $1.44 \text{ \AA}$  and  $1.88 \text{ \AA}$ . The cell parameters can only decrease if the radii of the void cation decreases. This indicates the replacement or substitution of Cs by Sr in the voids of the pollucite matrix.

The representative of this series for  $x=0.8$  was heat treated at  $1000^\circ\text{C}$ . The results are shown in figure 9.

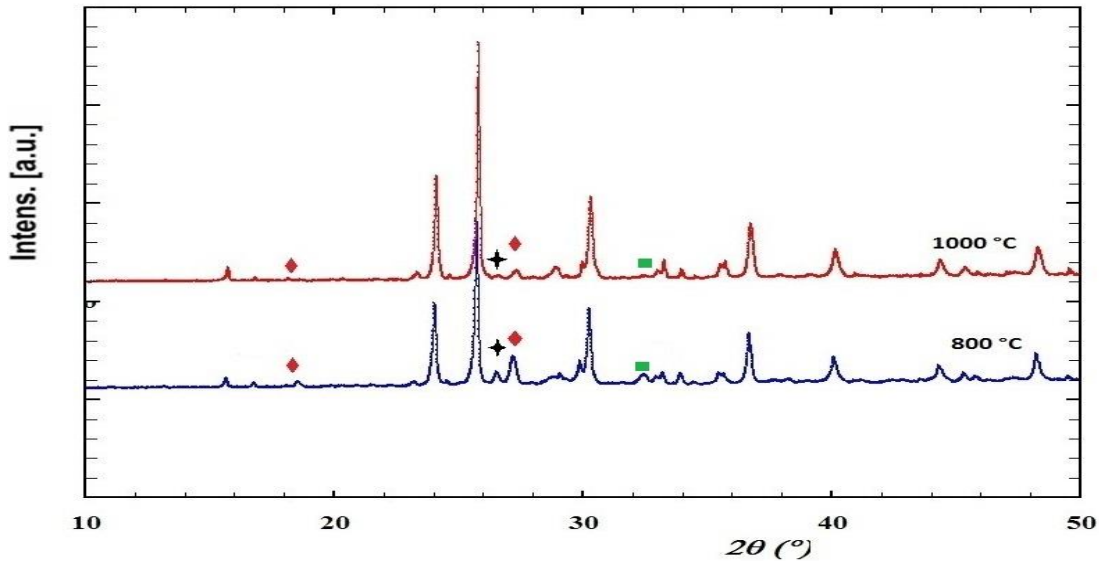
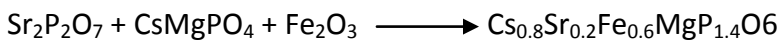


Figure 9 The diffractogram for  $x=0.8$  after 800 °C and 1000 °C.  $\blacklozenge$  =  $\text{Sr}_2\text{P}_2\text{O}_7$ ,  $\blackstar$  =  $\text{CsMgPO}_4$  and  $\blacksquare$  =  $\text{Fe}_2\text{O}_3$

After a heat treatment of 1000 °C the peaks of  $\text{Sr}_2\text{P}_2\text{O}_7$ ,  $\text{CsMgPO}_4$  and  $\text{Fe}_2\text{O}_3$  become significantly less intense, which could indicate a reaction between these compounds to form pollucite, for example:

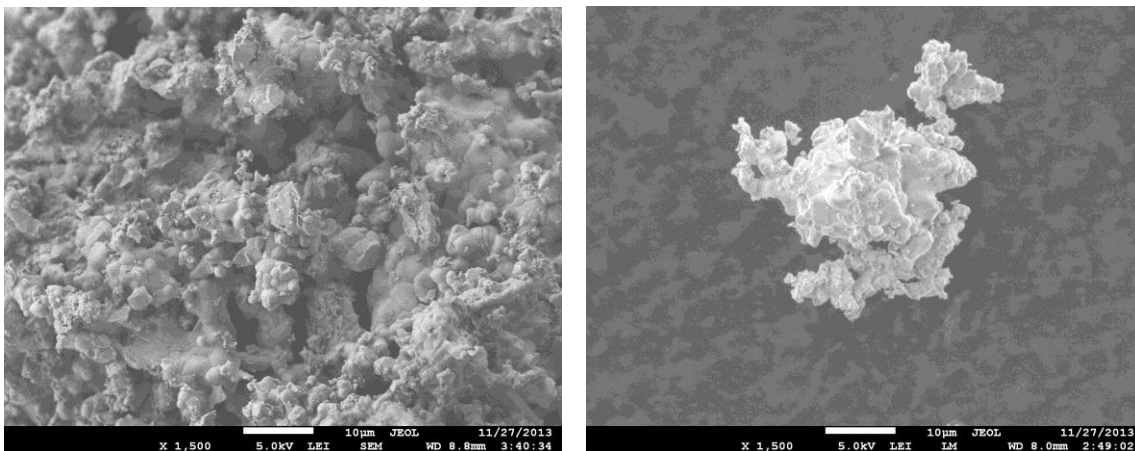


While the amount of the secondary phases decrease, the main phase's peaks become more intense. This means that at higher temperature the sample becomes more crystalline and pure.

The cell parameters of this sample decreases from 13.8519 Å to 13.8169 Å after heated from 800 °C to 1000 °C. There could be several reasons behind this. It could be that the smaller Sr is inserted in the pollucite matrix. Or symmetry changes could have occurred. A SEM-EDS analysis was done for  $x=0.8$  of the series  $\text{Cs}_x\text{Sr}_{(1-x)} [\text{Fe}_{(1-0.5x)}\text{MgP}_{(1+0.5x)}\text{O}_6]$  after 1000 °C to determine the exact composition. According to the XRD pattern  $\text{Sr}_2\text{P}_2\text{O}_7$  was also present in the sample.

The SEM images of this sample are given in figure 10 below.





**Figure 10 SEM images for  $x=0.8$  of the series  $Cs_xSr_{(1-x)} [Fe_{(1-0.5x)}MgP_{(1+0.5x)}]O_6$  after  $1000\text{ }^\circ\text{C}$**

This sample was red-brown. The micrographs show that smaller particles are agglomerated on bigger particles of about 20 to 40  $\mu\text{m}$ . The smaller particles size were in the order of 10  $\mu\text{m}$ .

With EDS two spot measurements and a semi-quantitative analysis were done and the composition of each element was calculated. The results were  $Cs_{1.07}Sr_{0.06} [Fe_{0.54}Mg_{0.96}P_{1.45}O_6]$  and  $Cs_{0.62}Sr_{0.33} [Fe_{0.6}Mg_{0.95}P_{1.40}O_6]$  on those spots. These results show that Cs and Sr are not distributed equally over the whole sample. The pollucite structure is an average of different compositions, detected by the XRD. The  $Sr_2P_2O_7$  was not analyzed. To obtain more accurate data the sample's surface should be flat, homogeneous and polished. But the data indicates the average Cs/Sr ratio which is close to the pollucite type of structure. A similar phenomena, where the same compositions gave different structures, occurred for  $Na_3BiO_4$  in (Vensky *et al.*, 2005).

The diffractogrammes of the compounds of  $Cs_xSr_{(1-x)} [Fe_{(0.5+0.5x)}Li_{(1-0.5x)}P_{1.5}O_6]$  at  $800\text{ }^\circ\text{C}$  for  $x=0, 0.2, 0.4, 0.6, 0.8$  are given in figure 11. These compounds were synthesized with the sol-gel method.

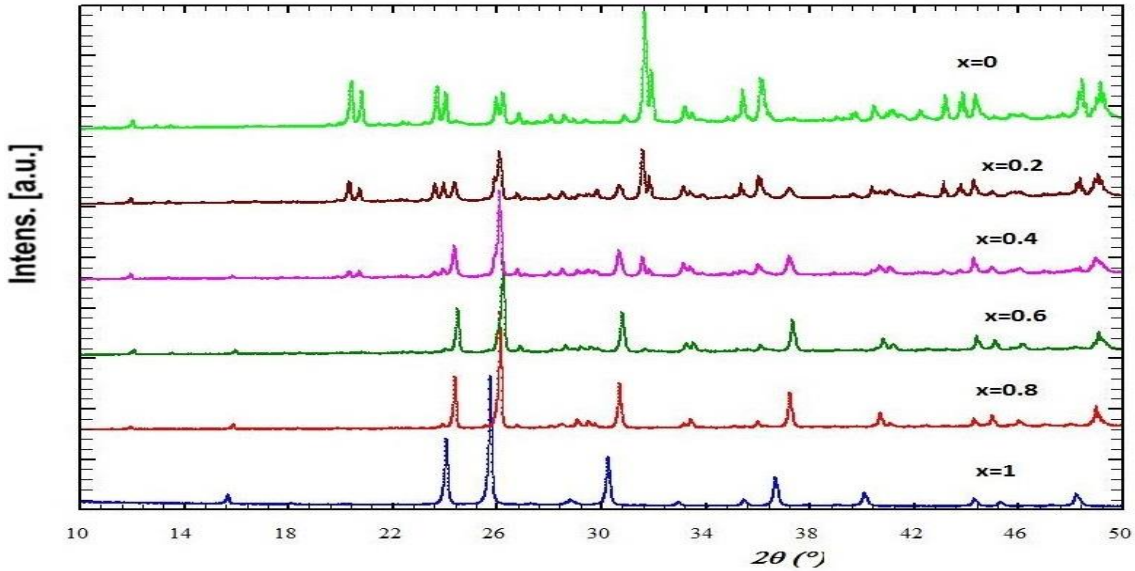


Figure 11 XRD data for  $\text{Cs}_x\text{Sr}_{1-x} [\text{Fe}_{(0.5+0.5x)}\text{Li}_{(1-0.5x)}\text{P}_{1.5}\text{O}_6]$ , 800°C,  $x=0, 0.2, 0.4, 0.6, 0.8, 1$

This data indicates that up till 60% of Sr in the void, the pollucite structure was formed, although some impurities were detected. There is only 40% of Sr present in the product waste stream after co-extraction, which is already obtained from this series of compositions. For  $x=0.8$  and  $0.6$  the structure of the formed compound is two-phased: pollucite and  $\text{Sr}_2\text{P}_2\text{O}_7$ . For  $x=0.4$ , there were also other admixtures. With only strontium in the matrix ( $x=0$ ),  $\text{Sr}_2\text{P}_2\text{O}_7$  is one of the main phases, but Fe and Li could not be identified.

The cell parameters were investigated and are shown in figure 12.

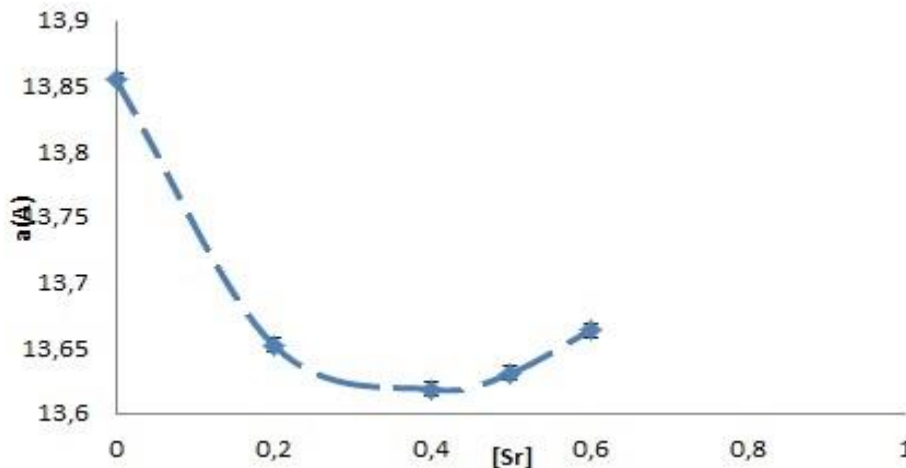


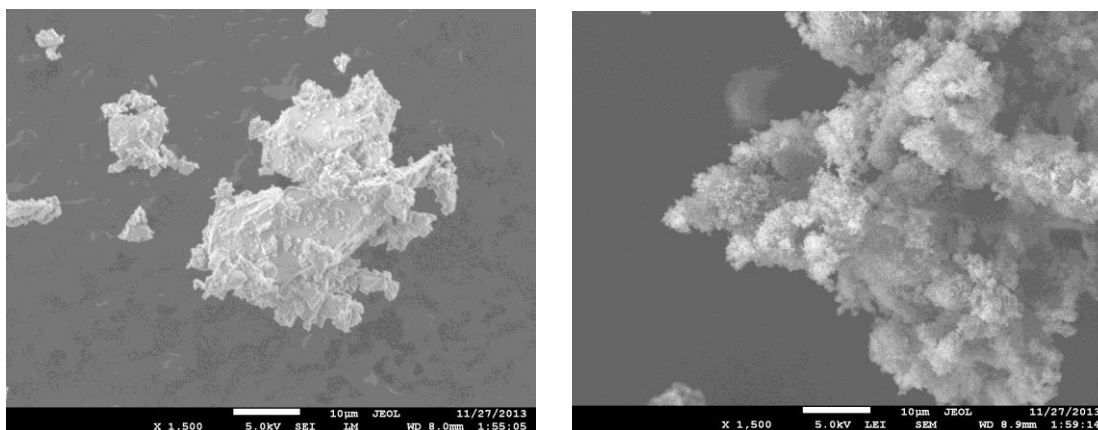
Figure 12 The cell parameters as a function of Sr for  $\text{Cs}_x\text{Sr}_{1-x} [\text{Fe}_{(0.5+0.5x)}\text{Li}_{(1-0.5x)}\text{P}_{1.5}\text{O}_6]$  after 800 °C

This data implies that for  $x= 0.6 - 1$  Sr has been included in the pollucite matrix, which led to the decrease of cell parameters. Below 40% of Sr in the void the cell parameters decrease dramatically. After  $x=0.4$  the cell parameter start to increase again. There are

several possible reasons for this behavior, which may lead to a symmetry change. The amount of structural sites might not be fully occupied in the pollucite crystal chemical formula  $T_{16}M_{24}[(T',T'')_{48}O_{96}]$ , which can cause structure modifications. Above all, the amount of strontium for  $x=0.5, 0.4$  may not be the actual amounts in the pollucite matrix, because the sample was not pure. Further investigations are required to understand this behavior, for example SEM-EDS or Mössbauer Spectroscopy.

For  $x=0.6$  a SEM analysis was done. The two expected compositions were  $Cs_{0.6}Sr_{0.4}[Fe_{0.8}Li_{0.7}P_{1.5}O_6]$  and  $Sr_2P_2O_7$ . This sample could not be completely analyzed by EDS, because Li cannot be detected due to its low X-rays. But the Cs/Sr ratio could be determined, which was 57.1/31.3 mole %. This amount of Sr in the void of pollucite is close to the amount of Sr after co-extraction.

The SEM images are shown in the figure 13 below.



**Figure 13 SEM images for  $x=0.6$  of the series  $Cs_xSr_{(1-x)} [Fe_{(0.5+0.5x)}Li_{(1-0.5x)}P_{1.5}O_6]$  after  $800^\circ C$**

The sample was light brown. These micrographs show that smaller particles of about 2-5  $\mu m$  were agglomerated on bigger particles.

Based on table 1, formula compositions of pollucite compounds with only Sr in the structure were suggested. The synthesis was done with solid-state method at  $800^\circ C$ . The compounds were synthesized with framework cations, such as  $A=Li$ ;  $B=Mg, Ni$ ;  $R=Fe, B$ ;  $M=Si, Ti$ . These cations were chosen according to their radii difference within the 15% to make isomorphism possible. Cs has a bigger atomic radius than Sr, which means while exchanging Sr with Cs the total matrix becomes smaller. Therefore smaller interstitial cations were chosen along with Sr.

The results of the analysis of the phase analysis are shown in table 3.

**Table 3 Phase analysis results of phosphorus containing compounds with 100% Sr**

Targeted chemical formula	Phase analysis result
Sr[FeNiPO <sub>6</sub> ]	Fe <sub>3</sub> O <sub>4</sub> , (Sr <sub>0.85</sub> Ni <sub>0.153</sub> )(PO <sub>4</sub> ) <sub>2</sub>
Sr[Li <sub>0.5</sub> NiP <sub>1.5</sub> O <sub>6</sub> ]	LiNi(PO <sub>4</sub> ), (Sr <sub>0.85</sub> Ni <sub>0.153</sub> )(PO <sub>4</sub> ) <sub>2</sub>
Sr[SiLiPO <sub>6</sub> ]	Sr <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , Li <sub>3</sub> PO <sub>4</sub> , SrSiO <sub>3</sub>
Sr[Ni <sub>1.5</sub> Si <sub>0.5</sub> PO <sub>6</sub> ]	Ni <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , (Sr <sub>0.85</sub> Ni <sub>0.153</sub> )(PO <sub>4</sub> ) <sub>2</sub>
Sr[Li <sub>0.5</sub> Fe <sub>1.5</sub> PO <sub>6</sub> ]	(Sr <sub>0.85</sub> Zn <sub>0.15</sub> ) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (Sr-whitlockite), Fe <sub>2</sub> O <sub>3</sub>
Sr[Li <sub>0.5</sub> B <sub>1.5</sub> PO <sub>6</sub> ]	Sr <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , Li <sub>3</sub> PO <sub>4</sub> , Sr <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (BO <sub>3</sub> ) <sub>2</sub>

The results of the series Cs<sub>x</sub>Sr<sub>(1-x)</sub>[Fe<sub>(0.5+0.5x)</sub>Li<sub>(1-0.5x)</sub>P<sub>1.5</sub>O<sub>6</sub>] and Cs<sub>x</sub>Sr<sub>(1-x)</sub>[Fe<sub>(1-0.5x)</sub>MgP<sub>(1+0.5x)</sub>O<sub>6</sub>] showed that Sr could be inserted only partially in the pollucite matrix. Based on these results and data from table 1, new formula compositions of a Cs:Sr = 1:1 were synthesized. The synthesis was done with solid-state method at 800 °C.

In table 4 the results of the phase analysis of these compositions are shown.

**Table 4 Phase analysis results of phosphorus containing compounds with 50% Sr and 50% Cs in the expected structure of pollucite**

Chemical formula	Phase
Cs <sub>0.5</sub> Sr <sub>0.5</sub> [Fe <sub>0.75</sub> Li <sub>0.75</sub> P <sub>1.5</sub> O <sub>6</sub> ]	Pollucite, Li <sub>3</sub> PO <sub>4</sub>
Cs <sub>0.5</sub> Sr <sub>0.5</sub> [Si <sub>0.25</sub> Fe <sub>1.75</sub> PO <sub>6</sub> ]	(Sr <sub>0.85</sub> Si <sub>0.15</sub> ) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , CsFeP <sub>2</sub> O <sub>7</sub>
Cs <sub>0.5</sub> Sr <sub>0.5</sub> [Si <sub>0.75</sub> Ni <sub>1.25</sub> PO <sub>6</sub> ]	Sr <sub>2</sub> Ni(PO <sub>4</sub> ) <sub>2</sub> , Cs <sub>2</sub> SiO <sub>3</sub>
Cs <sub>0.5</sub> Sr <sub>0.5</sub> [Ti <sub>0.75</sub> Ni <sub>1.25</sub> PO <sub>6</sub> ]	Sr <sub>2</sub> Ni(PO <sub>4</sub> ) <sub>2</sub> , CsTi <sub>1.06</sub> P <sub>0.94</sub> O <sub>5</sub>

These results show that despite the formula compositions were chosen correctly, the pollucite structure did not form. This may have happened because of inhomogeneity while synthesis with solid-state or less favorable thermodynamic stability of the compounds. Other synthesis methods could also be tested.

Silicates with pollucite structure were also prepared. A previous study showed a complete solid solution series along the join Cs[AlSi<sub>2</sub>O<sub>6</sub>]- Cs[FeSi<sub>2</sub>O<sub>6</sub>] (*Mazza et al., 1997*). Cs[FeSi<sub>2</sub>O<sub>6</sub>] was synthesized with sol-gel and Pechini.

The series Cs<sub>x</sub>Sr<sub>(1-x)</sub> [Fe<sub>x</sub>Mg<sub>(1-x)</sub>Si<sub>2</sub>O<sub>6</sub>] was synthesized for x=0, 0.2, 0.4, 0.6, 0.8 and 1.

The result for this series, synthesized with the sol-gel method, for x=1 at 600, 800 and 1000 °C is given in figure 14.

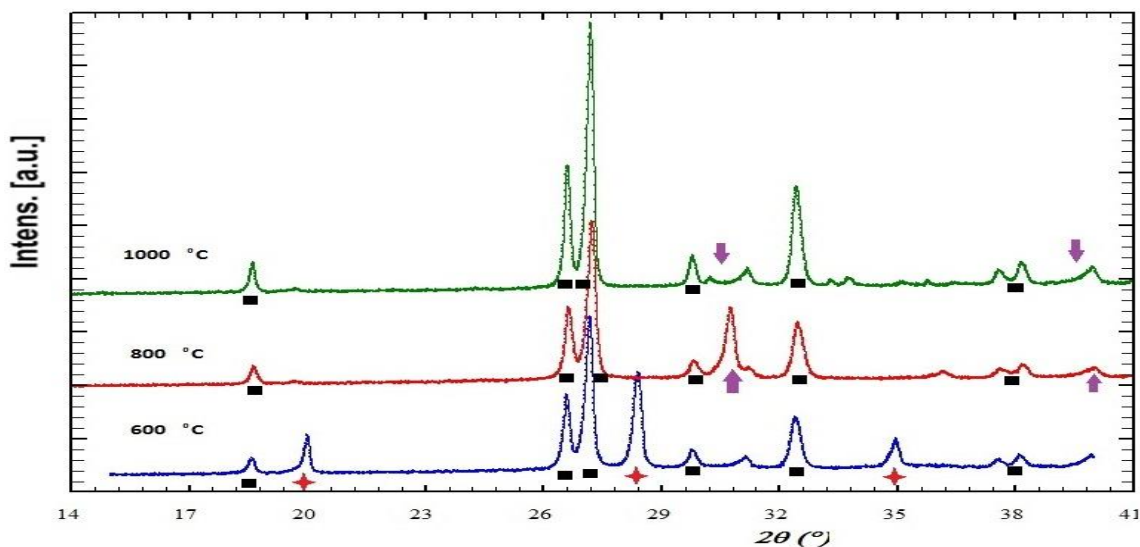


Figure 14 XRD pattern for  $x=1$  of the series  $\text{Cs}_x\text{Sr}_{(1-x)}[\text{Fe}_x\text{Mg}_{(1-x)}\text{Si}_2\text{O}_6]$  after heat treatments of 600, 800 and 1000 °C. ■ =  $\text{Cs}[\text{FeSiO}_4]$ , ★ =  $\text{CsNO}_3$  and ↑ =  $\text{SiO}_2$ .

This diffractogram (figure 15) shows that no pollucite structure was obtained.

At 600 °C two phases were present, namely the initial reagent  $\text{CsNO}_3$  and a  $\text{Cs}[\text{FeSiO}_4]$  phase. At higher temperatures the samples becomes more crystalline, while the unreacted  $\text{CsNO}_3$  disappears. At 800 °C the crystallization of  $\text{SiO}_2$  leads to the appearance of peaks at  $2\theta=30^\circ$ . The intensity of this peak at 1000 °C becomes smaller due to a phase transition of  $\text{SiO}_2$  from  $\beta$ -quartz to tridymite.

The XRD pattern of  $\text{Cs}[\text{FeSi}_2\text{O}_6]$ , synthesized with the Pechini method after a 800 °C heat treatment, is given in figure 15.

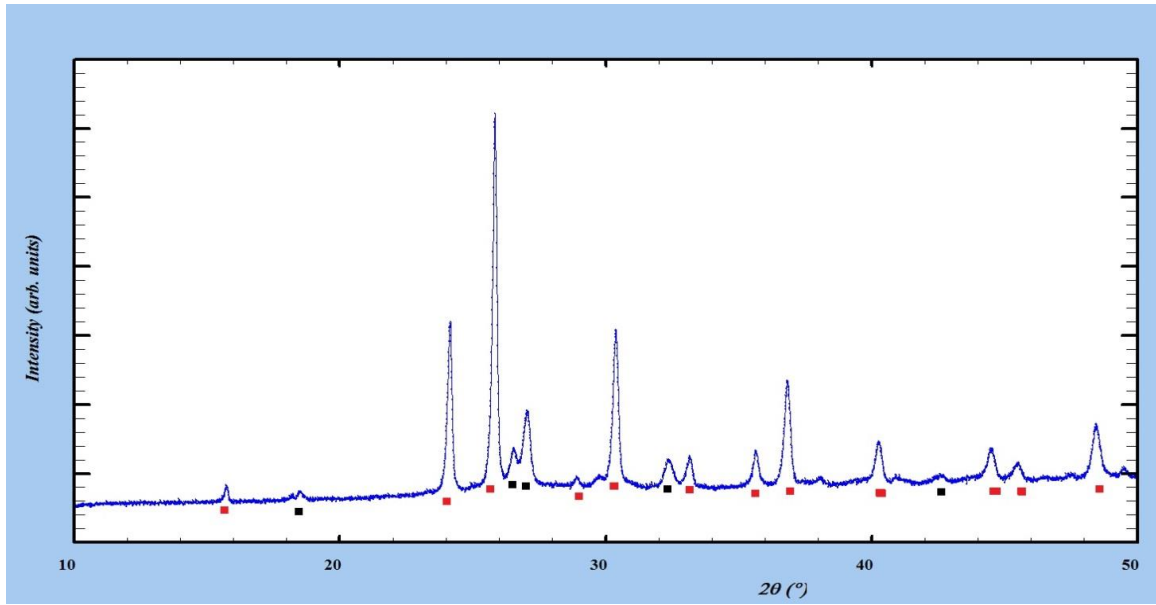


Figure 15 XRD pattern of  $\text{Cs}[\text{FeSi}_2\text{O}_6]$  at 800 °C. ■ =  $\text{Cs}[\text{FeSiO}_4]$  and ■ = Pollucite

This diffractogramme shows the main phase was pollucite. The secondary phase of orthosilicate ( $\text{Cs}[\text{FeSiO}_4]$ ) was the formed, which was obtained earlier with sol-gel (figure 7). There is a thermodynamic equilibrium between these two compositions, which can to be optimized to obtain a pure sample of pollucite.

## Conclusion

In this work the inclusion of Cs/Sr fraction in silicon and phosphorus based compositions with the pollucite structure were tested with different methods. 40% of Sr in one position in the void of pollucite matrix was already sufficient for a Cs/Sr inclusion in the waste form according to data from the co-extraction of cesium and strontium from HLW. Phosphorus based pollucites with Sr partially inserted in the matrix were successfully obtained with Mg and Li, along with Fe in the framework. These compounds were prepared with the sol-gel method. Silicon based pollucite was only formed with the Pechini method. The results showed that a certain type of method can have a big influence on the product that is formed.

## Future work

In the future synthesis with other methods should be tried, for example the ball-milling method. This method uses a ball mill to grind material into fine powder. It consists of a cylindrical shell rotating about its axis with a grinding medium (balls). This method is interesting, because of the small particle sizes and extensive surface area that could be obtained. Spark Plasma Sintering (SPS) is also an interesting application for the fabrication of ceramics. This a pressure sintering method based on high temperature plasma.

Synthesis with different methods can be used to aim for a compound with 100% strontium in the pollucite matrix.

If in the future a pure compound with a Cs:Sr = 60:40 mole% is obtained, different characterization techniques on the properties can be applied, namely the Mössbauer spectroscopy to study the iron tetrahedral sites in pollucite, investigation of leaching rates, thermal stability and thermal expansion.

Other structure types except pollucite may also be interesting which may be formed more easily with a Cs/Sr fraction, for example the NZP structure type ( $\text{NaZr}_2(\text{PO}_4)_3$ ).



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