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A Reitveld quantitative XRD phase-analysis of selected composition of the $Sr_{(0.5+x)}Sb_{(1-x)}Fe_{(1+x)}(PO_4)_3(0 < x < 0.50)$ system

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Abstract. Qualitative XRD phase-analysis of four ($x = 0.10$, 0.20, 0.30, 0.40) selected compositions of the $Sr_{(0.5+x)}Sb_{(1-x)}Fe_{(1+x)}(PO_4)_3(0 < x < 0.50)$ system was undertaken. XRD data shows the absence of a continuously solid solution. In fact, each composition is composed only of a mixture of the two end members, $Sr_{0.50}SbFe(PO_4)_3$ ($R\bar{3}$ space group) and $SrSb_{0.50}Fe_{1.50}(PO_4)_3$ ($R\bar{3}c$ space group), type-phases. Rietveld refinement method, using the XRPD technique, has been used for a quantitative phase-analysis of these compositions. In order to evaluate the relative errors of this experimental result, a set of standard phase-mixtures of both end compositions of the system was also quantified by the Rietveld method. Obtained results show the usefulness of this method for quantitative phase-analysis, particularly in geology including other classes of materials such clay and cement.

1. INTRODUCTION

The Nasicon-type family has been the subject of intensive research due to its potential applications as solid electrolyte, electrode material, low thermal expansion ceramics and as storage materials for nuclear waste [1–6] The structure of such materials with general formula $A_xXX'(PO_4)_3$ consists of a three-dimensional network made up of corner-sharing $X(X')O_6$ octahedra and PO_4 tetrahedra in such a way that each octahedron is surrounded by six tetrahedra and each tetrahedron is connected to four octahedral. Within the Nasicon framework, there are interconnected interstitial sites usually labelled M1 (one per formula unit) and M2 (three per formula unit) through which A cation can diffuse, giving rise to a fast-ion conductivity [1,3,7] (Fig. 1). The four such sites per formula unit can be represented by the crystallographic $[M2]_3[M1]XX'(PO_4)_3$ formula. Each M1 cavity is situated between two $X(X')O_6$ octahedra along the c-axis. Six M2 cavities with eightfold coordination are located between the $[O_3X(X')O_3[M1O_3X(X')O_3\ O_3X(X')O_3]_\infty$ ribbons and surround the M1 cavity "Fig. 1". Recently, the structural characteristics by powder X-ray diffraction (XRPD) study using the Rietveld method for $A_{0.50}SbFe(PO_4)_3$ ($R\bar{3}$ space group) and $ASb_{0.50}Fe_{1.50}(PO_4)_3$ phases ($R\bar{3}c$ space group) (A = Ca, Sr) were realised [8,9]. In all $A_{0.50}\,SbFe(PO_4)_3$ samples, A^{2+} cations occupied principally one-half of the M1 3a sites and the Sb^{5+} and Fe^{3+} cations are orderly distributed within the $SbFe(PO_4)_3$ framework. In the $ASb_{0.50}\,Fe_{1.50}(PO_4)_3$ phases, the A^{2+} cations are located in the M1 sites whereas the Sb^{5+} and Fe^{3+} cations are statistically distributed within the Nasicon framework. In the $Ca_{(0.5+x)}Sb_{(1-x)}\,Fe_{(1+x)}(PO_4)_3(0 < x < 0.50)$ system, a qualitative phase-analysis of the XRPD patterns have clearly shown the absence of a continuously solid solution [8]. In fact, XRD spectra of selected compositions of this system is composed principally of their two end members $Ca_{0.50}SbFe(PO_4)_3$ ($R\bar{3}$ space group) and $CaSb_{0.50}Fe_{1.50}(PO_4)_3$($R\bar{3}c$ space group).

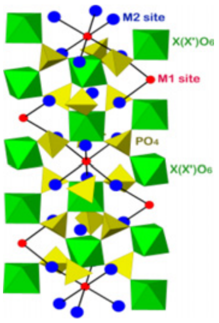

Figure 1. Crystal structure of the rhombohedral $[M2]_3[M1]XX'(PO_4)_3$ Nasicon-type.

In a continuation of our search concerning Nasicon-like structure, in this paper, we report the results of the structural characterisation of the $Sr_{(0.5+x)}Sb_{(1-x)}Fe_{(1+x)}(PO_4)_3$ system. As it will be shown in the following, this system is principally composed of a mixture of both end members $Sr_{0.50}SbFe(PO_4)_3$ and $SrSb_{0.50}\,Fe_{1.50}(PO_4)_3$ type-phases (abbreviated as $[Sr_{0.5}]$ and $[Sr_1]$ respectively). To our knowledge no most interest investigation on XRD Rietveld quantitative phase-analysis (RQXRD) within a biphasic system was reported. Herein, the Rietveld refinement methods was used as a tool for a quantitative phase-analysis of the four ($x = 0.10$, 0.20, 0.30, 0.40) selected compositions of the $Sr_{(0.5+x)}Sb_{(1-x)}Fe_{(1+x)}(PO_4)_3$ system.

2. EXPERIMENTAL

Syntheses of $[Sr_1]$, $[Sr_{0.5}]$ and four selected ($x = 0.10$, 0.20, 0.30, 0.40) compositions of the $Sr_{0(.5+x)}Sb_{(1-x)}\,Fe_{(1+x)}(PO_4)_3$ system were carried out using conventional solid-state reaction techniques. Powder crystalline samples were prepared from mixtures of carbonates $SrCO_3$ (Riedel-de Haën, 99%), oxides Sb_2O_3 (Riedel-de Haën, 99.9%), Fe_2O_3 (Prolabo, 99%) and $NH_4H_2PO_4$ (Riedel-de Haën, 99%) in stoichiometric proportions. The mixture was

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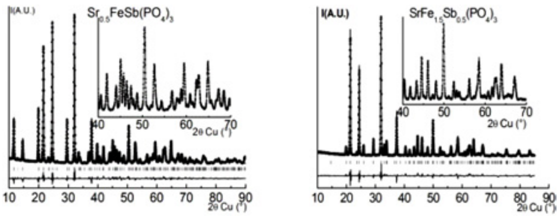

Figure 2. Experimental (• • •) calculated (—), and difference profile of the XRD pattern of $Sr_{0.50}SbFe(PO_4)_3$ and $SrSb_{0.50}Fe_{1.50}(PO_4)_3$ [9].

heated progressively with intermittent grinding at 200 °C (12 h), 400 °C (6 h), 600 °C (12 h), 800 °C (24 h), 900 °C (24 h) and 1000 °C (24 h) in air atmosphere. The products of reaction were characterised by X-ray powder diffraction (XRPD) at room temperature with a Panalytical X′ Pert-PRO (θ-2θ) diffractometer; (CuKα) radiation (45 kV, 40 mA); divergence slit of 1 ° and antiscatter slit of 1 °. The data were collected from 10 to 90° 2θ, in steps of 0.02°, with a counting time of 30 s per step. The Rietveld refinement of the structure was performed using the Fullprof program [10].

3. RESULTS AND DISCUSSION

If one wants to quantify the components of a complex mixture of solids, amongst resources which may be used is the Rietveld Quantitative X-ray Diffraction (RQXRD). Application of the Rietveld method to quantitative phase-analysis provides many advantages over traditional methods that utilize a small pre-selected set of integrated intensities. The power of this method, to quantitative phase-analysis is illustrated by a large number of papers on many different classes of materials [e.g., mineral, clay, cement,. . .] [11–18]. In fact, even if the Rietveld method offers superior performance over other methods such the RIR (Reference Intensity Ratio) method [14], recent report on the IUCR Round Robin study on quantitative-phase analysis indicates that accurate results may not always be obtained [19, 20]. As a conclusion of this latest studies it is obvious that it is of the utmost importance that the preparation of sample and specimen be appropriate for the task at hand. The second important point is the data collection, including appropriate wavelength.

Experimental and calculated XRD profile of both end members, $Sr_{0.50}SbFe(PO_4)_3$, abbreviated [$Sr_{0.5}$], and $SrSb_{0.50}Fe_{1.50}(PO_4)_3$, abbreviated [$Sr_1$], is shown in Figure 2. Since the positions of the main diffraction lines of the two XRD spectra of [$Sr_{0.5}$] and [Sr_1] are close, in the case of the four selected compositions of the $Sr_{(0.5+x)}Sb_{(1-x)}Fe_{(1+x)}(PO_4)_3$ system, we have shown only the representative area of the spectrum which is between 10 and 50 in two theta (Fig. 3).

Composition (x = 0.40) is isostructural to [Sr_1] phase but, as it was not expected, the XRPD patterns show that for compositions x with ($0 \leq x < 0.40$) only a biphasic system composed principally of both end, [$Sr_{0.5}$] and [Sr_1], type-phases exist (Fig. 3). It should be noticed that similar results are already obtained in the case of the $Ca_{(0.5+x)}Sb_{(1-x)}Fe_{(1+x)}(PO_4)_3$ ($0 \leq x \leq 0.50$) system [8].

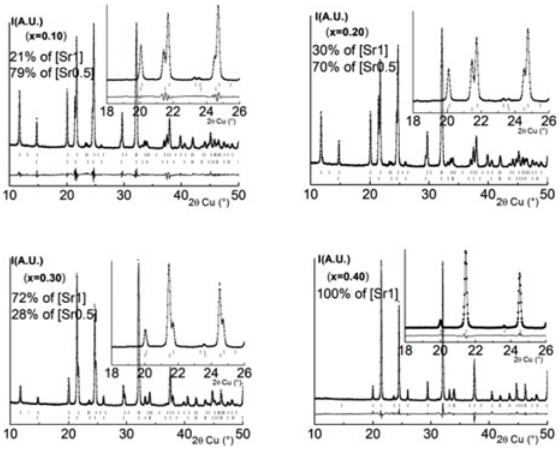

Figure 3. Experimental (• • •) calculated (—), and difference profile of the XRD pattern, in the 10–50° (2θ) range, of selected compositions of the $Sr_{(0.50+x)}Sb_{(1-x)}PFe_{(1+x)}(PO_4)_3$ system.

In order to clarify this assumption, a quantitative phase-analysis using the Rietveld method (RQXRD) of selected compositions of the $Sr_{(0.5+x)}Sb_{(1-x)}Fe_{(1+x)}(PO_4)_3$ system has been undertaken. In all cases, Rietveld refinement was carried out using a two-phase model, consisting of [$Sr_{0.5}$] and [Sr_1] Initial starting parameters for the Reitveld refinements of the four selected compositions of $Sr_{(0.5+x)}Sb_{(1-x)}Fe_{(1+x)}(PO_4)_3$ system were based upon the already above mentioned crystallographic results [9]. During the course of refinement, all variables parameters such atomic coordinates and cell parameter were allowed to vary. A relatively slight variation of the crystallographic parameters was observed and the obtained reliability factors were acceptable. Obtained molar phase fraction of the constituents, from the RQXRD analysis for each of both [$Sr_{0.5}$] and [Sr_1] type-phases, were indicated in Figure 3 for each composition.

It should be noticed that there is no direct relation between obtained molar phase fraction from RQXRD and the value of composition x in $Sr_{(0.5+x)}Sb_{(1-x)}Fe_{(1+x)}(PO_4)_3$ system. In fact obtained values of molar phase fraction should be dependant principally of the preparation route of every composition. Since The present study investigates accuracy and reliability of the RQXRD analysis at various molar phase fraction of the two ends, [$Sr_{0.5}$] and [Sr_1], type-phases, and in order to demonstrating the power of this method to analyse multiphase samples, a set of standard phase-mixture of the two, [$Sr_{0.5}$] and [Sr_1], materials have also been reported. The three standard binary mixtures of [$Sr_{0.5}$] and [Sr_1], with a molar fractions of (33% of [Sr_1], 66% of [$Sr_{0.5}$]) in (a), (50% of [Sr_1], 50% of [$Sr_{0.5}$]) in (b), and (66% of [Sr_1] 33% of [$Sr_{0.5}$]) in (c), were also mixed up and then analysed to assess the precision of Rietveld quantitative analysis. Note that synthetic materials were chosen for ease of assessment of results since the true concentration, of each phase within the mixture, is known from the molar phase fraction. Results of the Rietveld RQXRD analysis for the three standard selected mixtures of [$Sr_{0.5}$] and [Sr_1] are gathered in table 1. Observed and calculated XRPD patterns, in the 10–33° (2θ) range, of the three standard binary mixtures are shown in Figure 4.

Table 1. Results of the Quantitative Rietveld refinements analysis (RQXRD) of the three standard binary, $Sr_{0.50}SbFe(PO_4)_3$ [$Sr_{0.5}$] and $SrSb_{0.50}Fe_{1.50}(PO_4)_3$ [Sr_1], mixtures.

Prepared molar phase fraction mixtures	Obtained molar phase fraction (from RQXRD)	Estimated errors	Reliability factors
(a) 33% [Sr_1] 66% [$Sr_{0.5}$]	27% of [Sr_1] 71% of [$Sr_{0.5}$]	±7%	$R_B = 4.9\%$, for [Sr_1] $R_B = 4.9\%$, for [$Sr_{0.5}$]
(b) 50% [Sr_1] 50% [$Sr_{0.5}$]	45% of [Sr_1] 55% of [$Sr_{0.5}$]	±5%	$R_B = 5.0\%$, for [Sr_1] $R_B = 4.6\%$, for [$Sr_{0.5}$]
(c) 66% [Sr_{11}] 33% [$Sr_{0.5}$]	61% of [Sr_1] 39% of [$Sr_{0.5}$]	± 6%	$R_B = 5.6\%$, for [$Sr_{0.5}$] $R_B = 6.8\%$, for [Sr_1]

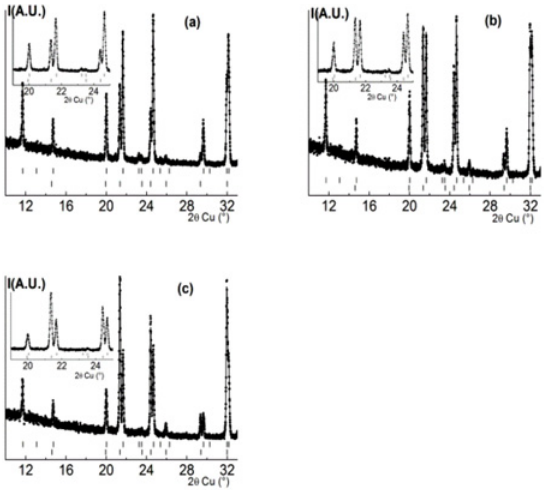

Figure 4. Experimental (• • •) and calculated (—) profile of the XRD pattern, in the 10–33° (2θ) range, of the three selected standard molar phase-mixtures: (33% of [Sr_1] and 66% of [$Sr_{0.5}$]) in (a), (50% of [Sr_1] and 50% of [$Sr_{0.5}$]) in (b) and (66% of [Sr_1] and 33% of [$Sr_{0.5}$]) in (c).

Close comparison between the experimental and theoretical molar phase fractions of standard mixtures, gives an estimated value of the relative error. Obtained relative error varies between 5 and 7% (Table 1).

4. CONCLUSION

RQXRD analysis of compositions consisting of a mixture of two phases that contain the same chemical elements was carried out. The Rietveld refinement protocol used in this study should find a wide application, on quantitative phases analysis, particularly in geology including other classes of materials such clay and cement. Reasonable accuracy is obtained however care must always be taken to ensure the physically meaningful values obtained from each refinement.

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