A Reitveld quantitative XRD phase-analysis of selected composition of the \( \text{Sr}(0.5+x)\text{Sb}(1-x)\text{Fe}(1+x)(\text{PO}_4)_3 \) \( (0 < x < 0.50) \) system

A. Aatiq, R. Tigha, A. Attaoui, N. Nadi and A. El Bouari

Laboratoire de Physico-Chimie des Matériaux Appliqués, Université HassanII-Mohammadia-Casablanca, Faculté des Sciences Ben M’Sik, Avenue Idriss El harti, BP. 7955, Casablanca, Morocco

Abstract. Qualitative XRD phase-analysis of four \( (x = 0.10, 0.20, 0.30, 0.40) \) selected compositions of the \( \text{Sr}(0.5+x)\text{Sb}(1-x)\text{Fe}(1+x)(\text{PO}_4)_3 \) \( (0 < x < 0.50) \) 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, \( \text{Sr}_0.5\text{SbFe}(\text{PO}_4)_3 \) \( (R \bar{3} \text{ space group}) \) and \( \text{SrSb}_0.5\text{Fe}_1.5(\text{PO}_4)_3 \) \( (R \bar{3}c \text{ space group}) \), 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 \( \text{A}_{XX'}(\text{PO}_4)_3 \) consists of a three-dimensional network made up of corner-sharing \( \text{X}(\text{X}')_6 \) octahedra and \( \text{PO}_4 \) tetrahedra in such a way that each octahedron is surrounded by six tetrahedra and each tetrahedron is connected to four octahedra. Within the Nasicon framework, there are interconnected interstitial sites usually labelled M1 (one per formula unit) and M2 (three per formula unit) through which \( \text{A} \) 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 \( \text{[M2]_3[M1]XX'}(\text{PO}_4)_3 \) formula. Each M1 cavity is situated between two \( \text{X}(\text{X}')_6 \) octahedra along the \( c \)-axis. Six M2 cavities with eightfold coordination are located between the \( \text{Sr}_{0.5+x}\text{Sb}(1-x)\text{Fe}(1+x)(\text{PO}_4)_3 \) \( (0 < x < 0.50) \) system.

In a continuation of our search concerning Nasicon-like structure, in this paper, we report the results of the structural characterisation of the \( \text{Sr}(0.5+x)\text{Sb}(1-x)\text{Fe}(1+x)(\text{PO}_4)_3 \) system. As it will be shown in the following, this system is principally composed of a mixture of both end members \( \text{Sr}_0.5\text{SbFe}(\text{PO}_4)_3 \) and \( \text{SrSb}_0.5\text{Fe}_1.5(\text{PO}_4)_3 \) type-phases (abbreviated as \( \text{Sr}_0.5 \) and \( \text{Sr}_1 \) 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 \( \text{Sr}(0.5+x)\text{Sb}(1-x)\text{Fe}(1+x)(\text{PO}_4)_3 \) system.

2. EXPERIMENTAL

Syntheses of \( \text{Sr}_1 \), \( \text{Sr}_0.5 \) and four selected \( (x = 0.10, 0.20, 0.30, 0.40) \) compositions of the \( \text{Sr}(0.5+x)\text{Sb}(1-x)\text{Fe}(1+x)(\text{PO}_4)_3 \) system were carried out using conventional solid-state reaction techniques. Powder crystalline samples were prepared from mixtures of carbones \( \text{SrCO}_3 \) (Riedel-de Haén, 99%), oxides \( \text{Sb}_2\text{O}_3 \) (Riedel-de Haén, 99.9%), \( \text{Fe}_2\text{O}_3 \) (Prolabo, 99%) and \( \text{NH}_4\text{H}_2\text{PO}_4 \) (Riedel-de Haén, 99%) in stoichiometric proportions. The mixture was
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 antisscatter 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 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 [Sr0.5] and [Sr1] type-phases, were indicated in Figure 3 for each composition.

In order to clarify this assumption, a quantitative phase-analysis using the Rietveld method (RQXRD) of selected compositions of the Sr0.5+xSb1−xFe1+x(PO4)3 system has been undertaken. In all cases, Rietveld refinement was carried out using a two-phase model, consisting of [Sr0.5] and [Sr1] Initial starting parameters for the Rietveld refinements of the four selected compositions of Sr0.5+xSb1−xFe1+x(PO4)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 [Sr0.5] and [Sr1] 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 Sr0.5+xSb1−xFe1+x(PO4)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 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 binary mixtures of [Sr0.5] and [Sr1], materials have also been reported. The three standard binary mixtures of [Sr0.5] and [Sr1], with a molar fractions of 33% of [Sr1], 66% of [Sr0.5] in (a), 50% of [Sr1], 50% of [Sr0.5] in (b), and 66% of [Sr1] 33% of [Sr0.5]) 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 [Sr0.5] and [Sr1] are gathered in table 1. Observed and calculated XRPD patterns, in the 10–50° (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.

<table>
<thead>
<tr>
<th>Prepared molar phase fraction mixtures</th>
<th>Obtained molar phase fraction (from RQXRD)</th>
<th>Estimated errors</th>
<th>Reliability factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 33% [Sr$<em>1$] 66% [Sr$</em>{0.5}$]</td>
<td>27% of [Sr$<em>1$] 71% of [Sr$</em>{0.5}$]</td>
<td>±7%</td>
<td>$R_B = 4.9%$, for [Sr$<em>1$] $R_B = 4.9%$, for [Sr$</em>{0.5}$]</td>
</tr>
<tr>
<td>(b) 50% [Sr$<em>1$] 50% [Sr$</em>{0.5}$]</td>
<td>45% of [Sr$<em>1$] 55% of [Sr$</em>{0.5}$]</td>
<td>±5%</td>
<td>$R_B = 5.0%$, for [Sr$<em>1$] $R_B = 4.6%$, for [Sr$</em>{0.5}$]</td>
</tr>
<tr>
<td>(c) 66% [Sr$<em>{11}$] 33% [Sr$</em>{0.5}$]</td>
<td>61% of [Sr$<em>1$] 39% of [Sr$</em>{0.5}$]</td>
<td>±6%</td>
<td>$R_B = 5.6%$, for [Sr$<em>1$] $R_B = 6.8%$, for [Sr$</em>{0.5}$]</td>
</tr>
</tbody>
</table>

![Figure 4](image-url) 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.

References