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# Holistic RBS–PIXE data reanalysis of SBT thin film samples

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**Abstract**

The growth of $SrBi_2Ta_2O_9$ (SBT) films on top of Pt electrode substrates is an important issue for the fabrication of ferroelectric based memories. In a recent publication, SBT thin films grown using seeded and unseeded procedures were studied by PIXE and RBS. Difficulties and misfits found in the comparison of results from both techniques were, at that time, overcome by physical considerations. These, although not rendering interpretation impossible, left out the possibility of understanding the exact nature of the differences between the interface behavior in each case. In the present work it is shown that the reanalysis of the same data using the recently developed RBS–PIXE simultaneous and self-consistent calculation present in NDF leads to stronger conclusions on the solid state reaction occurring during the deposition stage for both types of samples. Allowing for the occurrence of solid state reactions between the deposited film and the Pt electrode even in the case of seeded samples leads to a full explanation of IBA data, this result showing that in complex systems such as this, the PIXE data are essential and must be integrated with the RBS data in an holistic analysis, in order to properly unfold the depth profile of the samples. Contrary to what is usually supposed PIXE data is therefore shown to contain hidden depth structure information.
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## 1. Introduction

$SrBi_2Ta_2O_9$ (SBT) is a Bismuth Layered Perovskite (BLP) with interesting ferroelectric properties for memories applications. A previous study on the synthesis of seeded and unseeded SBT thin films by some of the authors [1] showed that increase of the film crystallinity and improvement of the thin film ferroelectric properties were a result of the use of SBT seeds. Details on the role of the seeds as an improver of the thin film properties were then investigated [2], and it was concluded that the films synthesized without SBT seeds show the formation of an interface of variable content and/or shape, while the use of the seeds contributes to a higher stability of the film and electrode constituents. An inhibition effect of the seeds regarding interface reactions was then inferred and converted in the assumption that the seeds act as a barrier preventing the inter-diffusion between the SBT film and the Pt-layer. As a result, a better preservation of the thin film composition and the enhanced electrical properties was observed.

In the present work a thorough reanalysis of the IBA data on two of the previously studied samples was carried out by using the routine for self-consistent analysis of the RBS and PIXE data [3,4] recently made available in the NDF code [5]. One of the most important results achieved and shown here is that requiring that the PIXE results are

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well simulated imposes important restrictions onto the depth structure of the samples, even though PIXE is usually considered as a technique which carries no depth structure information. This hidden information, which can only be assessed by self-consistent analysis of RBS and PIXE spectra, leads to slight changes in the interpretation of the IBA data on the SBT seeds effect.

## 2. Materials and methods

As presented before in detail [1,2], seeded and unseeded SBT films were prepared by spin-coating organic solutions of the required cations on $Si/SiO_2/Ti/Pt$ substrates followed by heat treatment at adequate temperatures. Different cation proportions were selected so as to obtain nominal stoichiometric and non-stoichiometric (Bi-deficient) compositions. For seeded films, seeds were previously deposited by spin-coating on the substrate. The details of the experimental procedures have been published elsewhere [1]. Table 1 identifies the samples used in the current work. The film crystalline structure was analyzed by grazing incidence X-ray diffraction (Philips X'Pert MPD X-ray diffractometer with CuKα radiation), which confirmed the crystalline perovskite structure of all the prepared films without any second phases. RBS (Rutherford Backscattering Spectrometry) and PIXE (Particle Induced X-Ray Emission) analyses were performed using the 2.5 MV Van de Graaff Accelerator of ITN. RBS spectra were obtained with 2 Schottky barrier detectors placed in IBM geometry at 140° and 180° scattering angles, with resolutions of 15 and 25 keV respectively, using a 2.250 and a 2 MeV $He^+$ beam. Analysis were performed with samples tilted at 0°, 20° or 30° (angle between beam direction and sample normal). PIXE measurements were performed with a 2.15 MeV $H^+$ beam and the X-rays were detected with a Gresham Scirus detector with 155 eV energy resolution placed at 110° to beam direction and at a distance of 25 mm from the samples. The PIXE spectra were deconvoluted using the AXIL code [6]. Both PIXE and RBS data were simulated using the NDF code [5].

## 3. Results and discussion

In the RBS spectra of the seeded sample (Fig. 1), the Sr, Bi and Ta backscattering signals appear convoluted, thus impairing an independent determination of the Ta, Sr and Bi concentrations from these spectra. To overcome this shortcoming, the samples were also analyzed by PIXE.

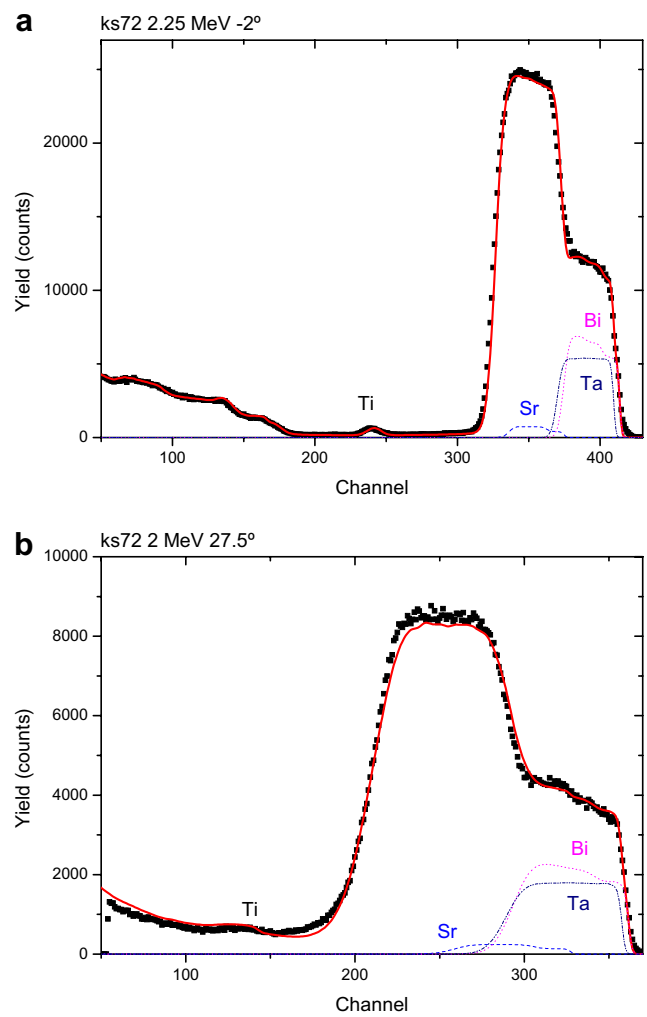


Fig. 1. RBS data and fit for sample S72 using a pure seed plus film model for different irradiation conditions: (a) $He^+$ of 2.25 MeV and 2° target tilt, and (b) $He^+$ of 2.0 MeV and 27.5° target tilt. It can be seen that the details in spectra (a) and (b) are not completely reproduced by the fit. Still, based only in RBS data, or even in RBS plus PIXE Sr, Ta and Bi data, improvement to this fit is hardly achievable.

Using the DATTPIXE code [5] in the analysis of PIXE data, the Pt results obtained from PIXE are found to be inconsistent with the RBS results for all divisible sample structures. Nevertheless, based on DATTPIXE results, and introducing the Ta/Sr and Bi/Sr PIXE ratios into the RBS simulations, the RBS spectra can be simulated if one of the following hypotheses is valid: (1) the Bi and/or Ta composition increases with depth; or alternatively, (2) a Pt/SBT film intermixing occurs. The second hypothesis

Table 1
Identification of the studied thin films

| Sample code[a] | Heat treatment temperature | Seeds | Nominal composition | | Simulation results | | | Ta-normalized results | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Sr | Bi | Sr | Bi/Sr | Ta/Sr | Sr | Bi |
| U72-2.0 | 720° | No | 1.0 | 2.0 | 1.0 | 1.9 | 2.0 | 1.0 | 2.0 |
| S72-2.0 | 720° | yes | 1.0 | 2.0 | 1.0 | 2.0 | 1.9 | 1.0 | 2.1 |

[a] S stands for seeded; U stands for unseeded and results using PIXE and RBS data from separate analysis.

is consistent with a process of Pt diffusion towards the surface, interface roughness or a solid state reaction between the Pt and any of the elements in the $SrBi_2Ta_2O_9$ film. Furthermore, the PIXE results for the Ta/Sr and Bi/Sr ratios were comparable to a nearly nominal composition for both samples, as shown in Table 1.

In a reanalysis of data using the NDF code which allows a holistic PIXE and RBS data analysis, a first approach was taken to the analysis of sample S72 by imposing a $SrBi_2Ta_2O_9$ stoichiometry for the seed, while the composition of the film was allowed to change. In detail a first deeper layer with the film nominal stoichiometry was forced, and two top layers with changed compositions were fitted. This was enough to reproduce the RBS data as shown in Fig. 1. The result can be claimed good in spite of some small details in the data that are not really reproduced by the fit. Meanwhile, the corresponding PIXE data simulation obtained for this configuration, presented in Table 2, clearly shows that both Pt and Ti fit do not reproduce experimental results and are therefore not compatible with this depth structure description.

In order to overcome this inconsistence, it was necessary to consider that both Bi and Ta concentrations increase with depth, as this was the single solution found to introduce enough Ta in the film so that Pt X-rays were sufficiently absorbed in the SBT film in order to reproduce the experimental results. Ta increase in the film is required as this element preferentially absorbs Pt X-rays. Bi increase which can by itself justify RBS data slopes, is not enough to reproduce PIXE data due to the lack of preferential X-ray absorption for Pt X-rays. On the other hand, a simple Ta increase in depth is not compatible with RBS spectra shape. Preservation of the full RBS spectra shape and PIXE integrated X-ray yields, nevertheless, imply that two assumptions that were not included in the previous analysis work are made here: (1) solid state reactions taking place between the seed and the Pt electrode lead, in the case of sample S72, to the formation of a layer of $200 \times 10^{15}$ at/cm$^2$ (roughly 37 nm at $5.46 \times 10^{22}$ at/cm$^3$ density) with a composition of $Pt_{11}Bi_5Ta_4$, and on top of which is an almost pure seed layer of $264 \times 10^{15}$ at/cm$^2$ (roughly 62 nm at $4.1 \times 10^{22}$ at/cm$^3$ density); and (2) on the film, located on top of the seed (which structure is presented in Table 3, corresponding RBS fits in Fig. 2), a composition gradient is inferred where Sr and O concentrations increases, while Ta and Bi concentrations decrease. The current detailed analysis thus lead to a result inverse to that inferred in the previous analysis, as a loss of stoichiometry is now infered to be present in the deposited film when going from the seed interface towards the surface. A small contamination of K and Ca in the ratio of 5:1 can also be infered to be present in both film and seed (this fact was not considered in the previous analysis either). The deep $TiO_2$ film presents an apparent V contamination, this single justification found to reduce the difference between simulated and observed PIXE data for Ti, compatible with

Table 2
PIXE simulated (fit) and observed (data) X-ray counts results using the holistic routine in NDF and preserved seed

| S72-2.0 | Data | Error | Fit |
|---|---|---|---|
| Sr | 3153 | 57 | 3206 |
| Bi | 16,657 | 131 | 16,921 |
| Ta | 38,950 | 3470 | 37,387 |
| Pt | 63,000 | 252 | 94,298 |
| Ti | 724 | 32 | 2055 |

The error stated is the absolute error inferred from AXIL error output.

Table 3
Top layer composition using NDF and a changed seed composition

| Thickness in $1 \times 10^{15}$ at/cm$^2$ | Sr | Bi | Ta | O |
|---|---|---|---|---|
| 420 | 9.0 | 12.3 | 12.3 | 65.9 |
| 420 | 8.0 | 13.1 | 13.1 | 65.3 |
| 420 | 7.1 | 14.4 | 14.4 | 63.7 |

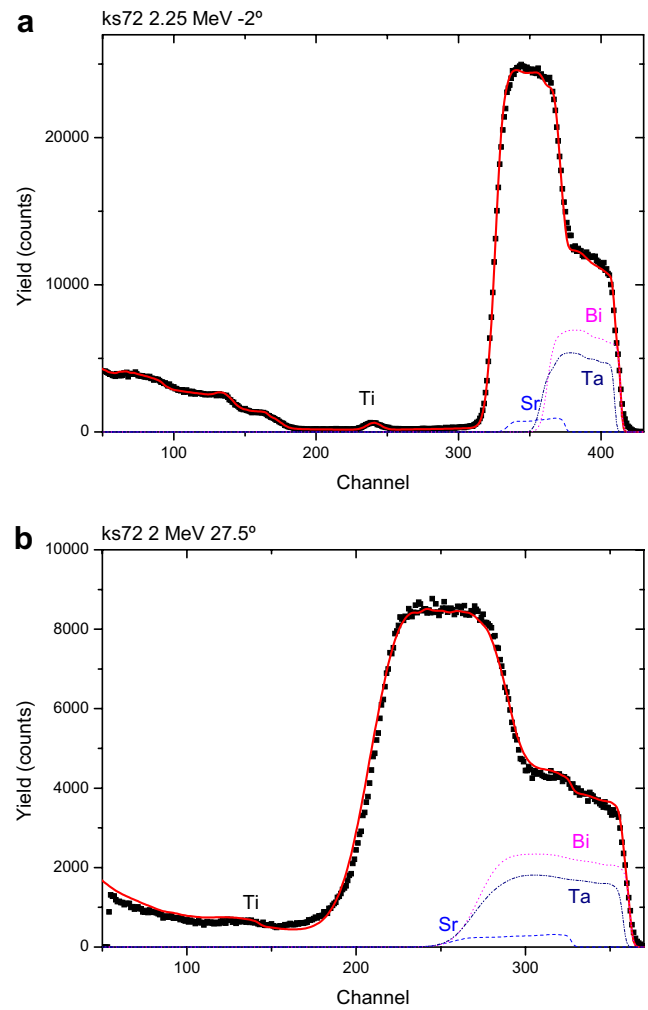


Fig. 2. RBS data and fit for sample S72 for different irradiation conditions: (a) $He^+$ of 2.25 MeV and 2° target tilt, and (b) $He^+$ of 2.0 MeV and 27.5° target tilt. Using a model that assumes Pt–Bi and Pt–Ta solid state reactions between seed and Pt electrode, and loss of stoichiometry towards the surface of the SBT film, a better agreement is achieved between simulation and data in the RBS spectra.

Table 4
PIXE simulated (fit) and observed (data) X-ray counts results using the holistic routine in NDF and changed seed

| S72-2.0 | Data | Error | Fit |
|---|---|---|---|
| Sr | 3150 | 57 | 3179 |
| Bi | 16,657 | 131 | 16,281 |
| Ta | 38,950 | 3470 | 31,220 |
| Pt | 63,000 | 252 | 59,739 |
| Ti | 724 | 32 | 1381 |
| V | 119 | 26 | 110 |
| K | 135 | 20 | 145 |
| Ca | 75 | 20 | 73 |

The error stated is the absolute error inferred from AXIL error output.

RBS data. The fitted PIXE results for this model are shown in Table 4. It can be seen that now except for the Ti data, the reproduction is quite good. The underestimation of Ta may be due to some small secondary flourescence enhancement not accounted for in the NDF model. The case of the overestimation of Ti is not so clear. The fact that it is present only in a quite deep layer and in a small quantity limits the capacity to determine some proper justifications for these misfits based only on the currently available data.

In the case of the unseeded sample, results qualitatively similar to the ones found using DATTPIXE were achieved although now both a zone of mixture (without roughness) and a zone of mixture or roughness are expected to be present. In the case of the U72 sample, the effects of the film deposition upon the Pt electrode are further seen to extended to the Pt–$TiO_2$ interface where mixing is now predicted.

The possibility of occurrence of solid state reactions between SBT elements and the Pt electrode was explored in detail in the previous work [2]. The present results further support their important role in the production of SBT ferroelectric thin films.

## 4. Conclusions

In previous work, SBT films synthesized without seeds were concluded to show the formation of an interface of variable content and/or shape. The use of seeds revealed itself as a contribution to a higher stability of the film and electrode constituents thus suggesting an inhibition effect of the seeds regarding solid state reactions in the Pt electrode interface. The present data analysis nevertheless shows that this inhibition may not be complete and that Bi–Pt and Ta–Pt reactions in seeded samples are required to fully explain results. In the case of the unseeded film an effect on the Pt–$TiO_2$ interface was inferred, which was not assumed previously. The importance of a full combined PIXE–RBS analysis in the case of complex systems such as this was thus shown to be quite important, not only for stoichiometric inference but, more than that, because depth information is preserved in the PIXE integral X-ray yields. In fact, the combined PIXE and RBS data can be seen as a integro-differential information on the sample under analysis, while the RBS is basically just differential data.

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