Experimental report

02/02/2018

Proposal: **5-23-689** **Council:** 10/2016

Title: Unveiling the oxide-ion diffusion in the new solid electrolytes Sr1-xKxSiO3 (x= 0.2, 0.4)

Research area: Materials

This proposal is a new proposal

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Samples: Sr1-xKxSiO3

Instrument	Requested days	Allocated days	From	To
D2B	2	2	03/02/2017	05/02/2017

Abstract:

The Sr1-xAxSiO3-0.5-delta (with A= Na, K) family has been proposed as a highly promising novel class of electrolyte materials showing good oxide-ion conductivity values at intermediate temperatures. However, there is some debate on the origin of the ionic conductivity in this system, perhaps arising from metastable glassy phases. Some studies showed that the Na occupancy on the Sr sites tended to zero while the oxygen sites tended to full occupancy. In contrast with these results, preliminary NPD refinements in test time on a carefully prepared Sr0.6K0.4SiO3-delta sample corroborated that the K occupancy on the Sr sites is significant and there is a conspicuous oxygen deficiency. Here we propose an "in situ" NPD study of Sr1-xKxSiO3-delta (x= 0.2, 0.4) compounds at high temperature, in the 25-1000ºC range, allowing us the refinement of accurate occupancy and thermal factors for the 5 unequivalent oxygen atoms in the unit cell, thus unveiling the oxygen diffusion path for this promising electrolyte.

The search for novel oxide-ion conductors has recently led to the identification of unusual candidates with suitable crystal structures. The system based upon $Sr(Si,Ge)O_3$ is appealing since the adequate doping at Sr sites provides the necessary oxygen vacancies with sufficient mobility at intermediate temperatures (500-700ºC), realized in the family $Sr_{1-x}A_xMO_{3-0.5x}$ (with A= Na, K; M = Si, Ge) [1]. K-doped samples in this system were subsequently shown to be highly hygroscopic at room temperature, while Na-doping was proved to be highly effective in introducing purely oxide ion conduction in the system [2,3]. Alkali doping, extending up to the composition $Sr_{0.55}Na_{0.45}SiO_{2.775}$, gives origin to a remarkable oxide ion conductivity ($\sigma \geq 10^{-2}$ S/cm^1 at T < 500 ºC) and is associated with a very low activation energy for oxide ion migration of about 0.3 eV. Based on such values, the $Sr_{0.55}Na_{0.45}SiO_{2.775}$ composition represents the best performing electrolyte material for SOFC currently known for temperatures lower than 650 ºC [3].

However, there is some debate on the origin of the ionic conductivity in this system. A recent study [4] on the structural and transport properties of the $Sr_{1-x}Na_xSiO_{3-0.5x}$ series (x = 0.05, 0.25, 0.45) concluded that the complexity of the SiO_2–Na_2O–SrO phase diagram had to be taken into consideration, as the actual solubility degree of Na in the $SrSiO_3$ phase should be significantly lower than expected due to the possibility of formation of secondary, spurious and metastable glassy phases, perhaps responsible for the promising transport properties for this class of materials. It also showed [4] that the Na occupancy on the Sr sites tended to zero (and the Sr site kept the full occupancy), while the oxygen sites tended to full occupancy.

The aim of the present experiment was to demonstrate that the alkali doping at the Sr sites indeed drives the formation of oxygen vacancies, and these are involved in the oxide-ion conduction across the solid. For this purpose we collected high-resolution neutron powder diffraction (NPD) data at the diffractometer D2B for $Sr_{0.6}K_{0.4}SiO_3$. The high intensity mode ($\Delta d/d \approx 5 \cdot 10^{-4}$) was selected, with a neutron wavelength λ= 1.594 Å within the angular 2θ range from 0° to 160°. About 2 g of the sample was contained in a cylindrical vanadium holder (dia. 8 mm), and the counting time was 4 h for each collection. The measurements were carried out in air at 298, 473, 673, 873 and 1073 K.

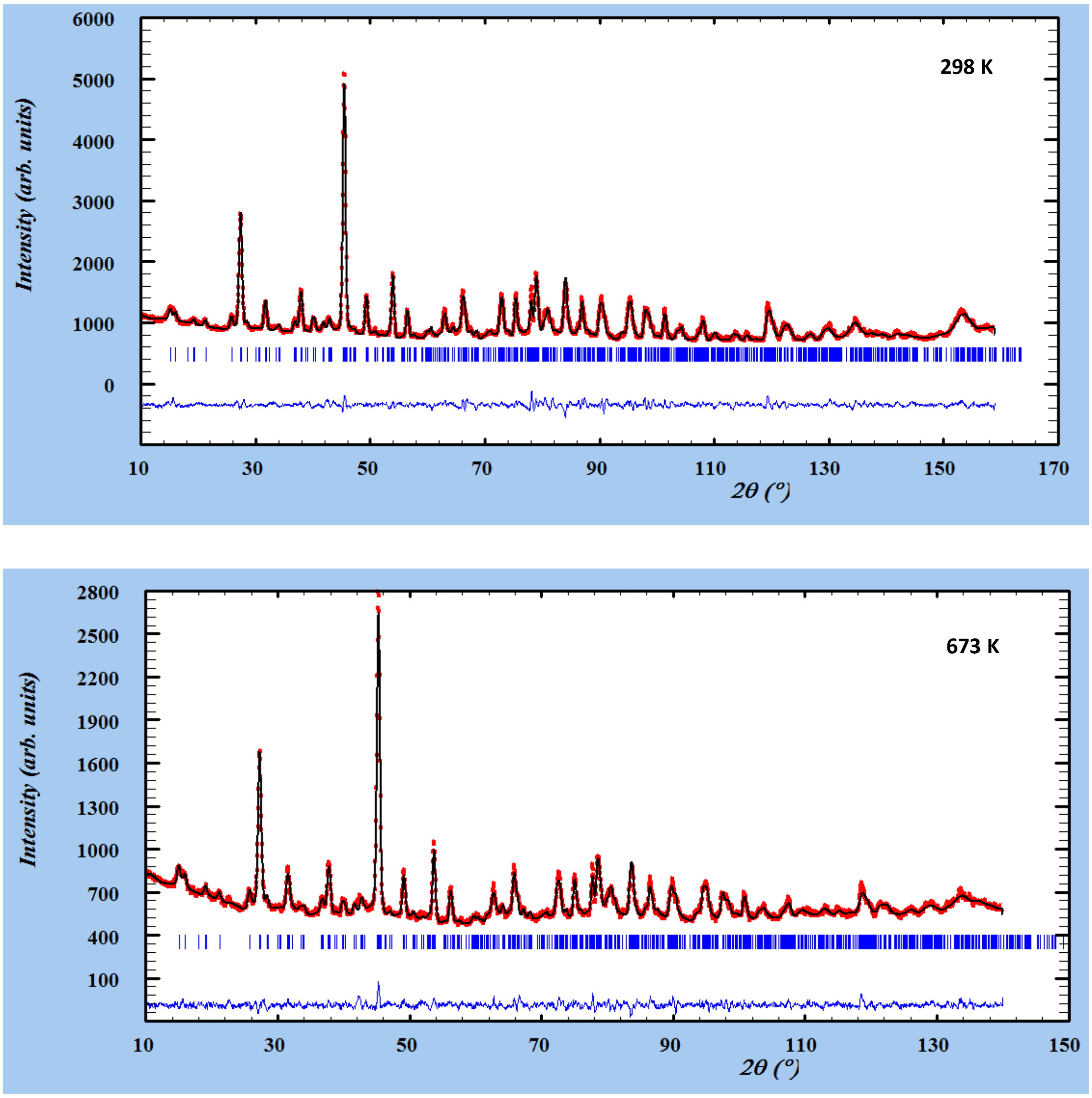

***Figure 1**. Rietveld refinement NPD profile for $Sr_{0.6}K_{0.4}SiO_3$ at 298 K and 673K. Observed (red crosses), calculated (black line), and difference (blue line).*

Fig. 1 illustrates the RT patterns of $Sr_{0.6}K_{0.4}SiO_3$ at 298 K and 673 K. The crystal structure can be Rietveld-refined in the monoclinic C2/c space group till 673 K. At higher temperature a phase segregation occurs, signalling the onset of phase decomposition. However, important information can be obtained from these refinements: K indeed enters into the crystal structure, heterogeneously distributed on the two available Sr1 and Sr2 sites, and a significant O deficiency is observed mainly on O3 and O4 oxygens. The refined stoichiometry at 298 K is $Sr_{0.83}K_{0.17}SiO_{2.75}\square_{0.25}$.

The crystal structure of $Sr_{0.6}K_{0.4}SiO_3$ consists of layers of Sr^{2+}/K^+ ions spaced by Si_3O_9 clusters, where each SiO_4 unit is linked through two corner oxygen ions to adjacent tetrahedra forming isolated three-fold rings. K substitution at the Sr2 site originates, for charge compensation, oxygen vacancies responsible for the oxide ion conductivity in the system [1,2]. Surprisingly, whereas $Si2O_4$ unit is an almost regular tetrahedron at RT, with 2xSi2-O3=1.67(1) Å and 2xSi2-O4= 1.62(1) Å bondlengths, however Si1O4 unit is better defined by an irregular trigonal pyramid with very long Si-O3 distances of 2.43(2) Å, accounting for the lability of this partially unoccupied oxygen atom. The remaining distances are reasonable: Si1-O1= 1.52(2) Å, Si1-O2= 1.51(2), Si1-O5= 1.85(2) Å. At 400ºC the $Si2O_4$ tetraedron slightly expands, showing longer distances to O3 of 1.70(1) Å, whereas Si1O4 tetraedron becomes more regular, by considerably shortening Si1-O3 distances to 2.06(4) Å; this trend also indicates that O3 oxygens are weakly bonded to both polyhedra, probably participating in the O motion across the structure.

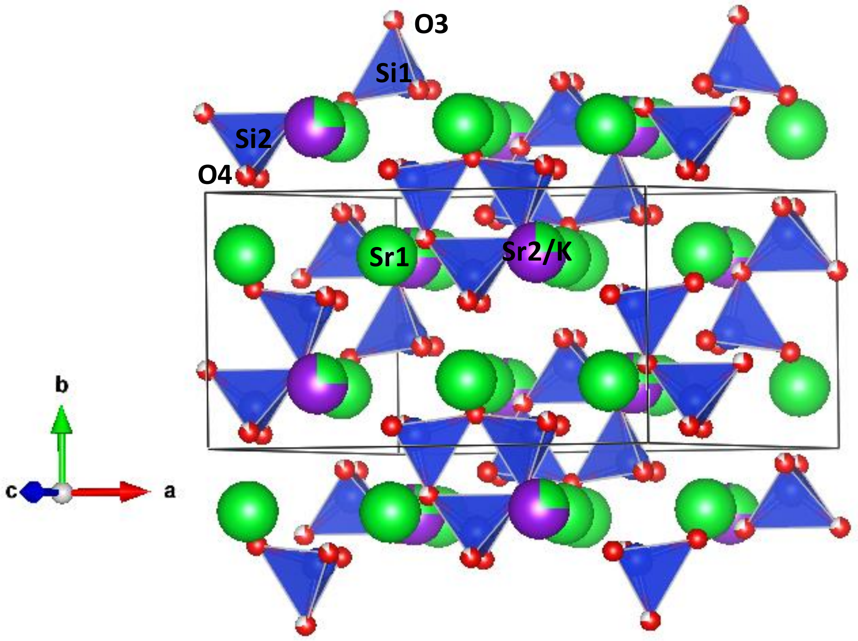

***Figure 2**. View of the crystal structure of $Sr_{0.6}K_{0.4}SiO_3$ at 400ºC, highlighting the existence of threefold rings of SiO_4 tetrahedra. O3 and O4 oxygen is partially unoccupied. K is occupying Sr2 positions.*

References

[1] P. Singh and J. B. Goodenough, Energy Environ. Sci., 2012, 5, 9626.
[2] P. Singh and J. B. Goodenough, J. Am. Chem. Soc., 2013, 135, 10149.
[3] T.Wei, P. Singh, Y. Gong, J. B. Goodenough, Y. Huang and K. Huang, Energy Environ. Sci., 2014, 7, 1680.
[4] C. Tealdi, L. Malavasi, I. Uda, C. Ferrara, V. Berbenni and P. Mustarelli, Chem. Commun., 2014, 50, 14732.