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Umbite Type Zirconium Germanates for Cs Removal

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ABSTRACT

Pure and Nb-doped zirconium germanate materials of composition $K_{2-x}Zr_{1-x}Nb_xGe_3O_9 \cdot H_2O$ where $x = 0, 0.1, 0.2$ and 0.3 with the structure of the natural mineral umbite have been prepared in high yield using hydrothermal synthesis methods. The parent material displays virtually no ion exchange of the K^+ for Cs^+ but the doped materials show rapidly enhanced exchange with replacement of ca. 70% of the K^+ by Cs^+ for the 30% doped material. Rietveld analysis of the powder X-ray diffraction data is consistent with no change in the unit cell parameters or K^+ bonding prior to the exchange, hence we propose the improved property is due to the creation of cation defect sites within the pores of the material that facilitates greater cation mobility and leads to exchange.

INTRODUCTION

Although aluminosilicate zeolites such as chabazite and clinoptilolite are still widely used for the removal of radioactive Sr^{2+} and Cs^+ from contaminated water, there is a growing use of other systems such as CST, Cs-treat and Sr-treat. For example, as part of the Fukushima clean-up efforts, IONSIV which is based on CST [1,2] has been used in the SARRY plant [3] and Cs-treat and Sr-treat are the active ion exchangers in the ALPS plant [4]. CST is a microporous titanosilicate with the sitinakite structure [2] and the optimized formula as used in IONSIV is $Na_{0.4}(H_3O)(Ti_{1.4}Nb_{0.6})O_3SiO_4 \cdot 2H_2O$ [5]. The two key chemical changes from the idealized parent formula of $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$ are replacement of 30% of the Ti^{4+} by Nb^{5+} followed by exchange of most of the Na^+ by H^+ to produce the acid form. Details of the exchange mechanism have been carefully and thoroughly elucidated to reveal why there is such a strong affinity for Cs^+ over H^+ [6].

Another family of materials that have been shown to be good for the same ion exchange reactions are based on the umbite structure, figure 1, and have a general composition of $M^I_2M^{IV}Si_3O_9 \cdot H_2O$ where M^I is a large monovalent cation such as K^+ or Na^+ and M^{IV} is a tetravalent cation that prefers octahedral coordination such as Ti^{4+} [7], Zr^{4+} [8] or Sn^{4+} [9]. A germanium form of the zirconium compound, $K_2ZrGe_3O_9 \cdot H_2O$, is also known [10]. To our knowledge, the ion exchange behavior of the zirconogermanate form has never been reported nor doped variants made. In this work we demonstrate that doping Nb^{5+} for Zr^{4+} up to levels of ca. 30% is possible in $K_2ZrGe_3O_9 \cdot H_2O$ with retention of the umbite structure. Furthermore, this doping leads to a dramatic improvement of the uptake of Cs^+ .

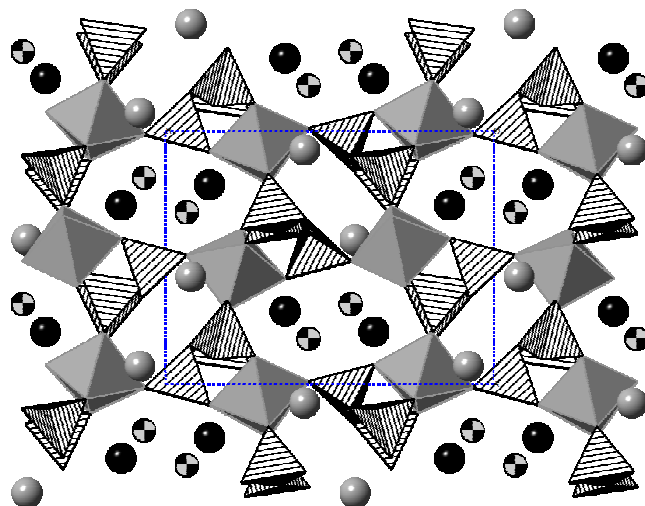


Figure 1. Umbite structure viewed down the c -axis showing how the framework is composed of corner-shared tetrahedral (hatched) and octahedral (solid) metals. There are two cation positions shown as grey and black spheres in the 6-ring and 8-ring tunnels, respectively, with the oxygen atoms of the water molecules that sit in the large pores shown as two-tone spheres.

EXPERIMENT

Synthesis of $K_2ZrGe_3O_9 \cdot H_2O \cdot H_2O$

The zirconogermanate umbite was prepared by mixing 1.52g of germanium dioxide (Gerald wise and Co.) and 1.66g of potassium hydroxide (85%, Sigma) in 20ml of deionised water. To the stirring mixture 1.50g of zirconyl chloride octahydrate (98%, Sigma) was added until dissolved. The mixture is then stirred for a further hour to allow it to homogenise. The resulting mixture was transferred to a 45ml Teflon liner and placed in a Parr autoclave at 200°C for 24 hours. The resulting product was then filtered and washed with deionised water before being dried overnight at 60°C.

Synthesis of $K_{2-x}Zr_{1-x}Nb_xGe_3O_9 \cdot H_2O$ where $x = 0.3$

The zirconogermanate umbite was prepared by mixing 0.76g of germanium dioxide (Gerald wise and Co.) and 0.85g of potassium hydroxide (85%, Sigma) in 10ml of deionised water. To the stirring mixture 0.19g of niobium chloride (99%, Sigma) was added with 0.52g of zirconyl chloride octahydrate (98%, Sigma). The mixture is then stirred for a further hour to allow it to homogenise. The resulting mixture was transferred to a 45ml Teflon liner and placed in a Parr autoclave at 200°C for 24 hours. The resulting product was then filtered and washed in deionised water before being dried overnight at 60°C.

X-ray powder diffraction

Any compounds synthesised were analysed using powder X-ray diffraction (XRD) on a Bruker D8 Advance using a Cu $K\alpha$ source at room temperature with data collected in transmission mode. Phase matching was performed using the EVA software from known databases. Long scans of ca. 4 hours were collected for Rietveld analysis and these were

absorption corrected using local software. Analysis then used the GSAS code [11] implemented with the EXPGUI interface [12].

Ion exchange studies

0.1 M solutions of caesium nitrate (99.8%, Sigma) were added to 0.2-0.5g of sample with an overall w/v ratio of 1:100. This was then shaken for 24 hours before being filtered and the solid was washed and dried overnight at 60°C. Elemental analysis was undertaken using X-ray fluorescence (XRF) on a Bruker S8 Tiger with the samples prepared as either a loose powder or pressed pellet. The measured weight percentages were converted to molar ratios and normalised to Ge.

DISCUSSION

The synthesis of $K_2ZrGe_3O_9 \cdot H_2O$ has been optimized as part of this work, and the procedure set out in the experiment section reproducibly makes ca. 2 g of material in ca. 80% yield. Doping with niobium is relatively straightforward up to ca. 30%, after that the formation of $HK_3Ge_7O_{16} \cdot 4H_2O$ (ICDD PDF pattern 04-009-9872) is observed. The powder X-ray diffraction patterns for the parent material and those doped with 10, 20 and 30 mole % niobium are shown in figure 2. It is noticeable that except for some peak broadening, presumably due to loss of crystallinity, very little else changes and there are no significant shift in peak positions indicating the unit cell dimensions are not affected by the doping. The presence of niobium was confirmed by XRF analysis which gave measured doping levels of 9%, 19% and 27%, respectively, table 1.

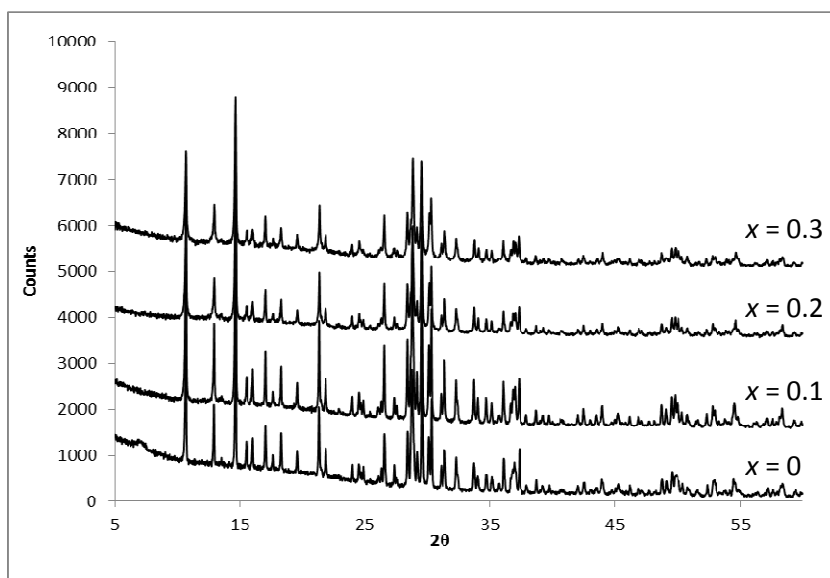


Figure 2. Powder X-ray diffraction patterns of $K_{2-x}Zr_{1-x}Nb_xGe_3O_9 \cdot H_2O$.

Ion exchange testing of the four materials was made using a 0.1 M Cs^+ solution with a 1:100 w/v ratio for 24 hours at room temperature. XRF analysis for the parent material showed negligible uptake whereas that for the doped materials was significantly improved, table 1, and the capacity of exchange for Cs clearly increases with the Nb content. Powder X-ray diffraction confirmed retention of most of the crystallinity and peaks characteristic of the umbite structure

but there are indications, currently under further investigation, that there may be a lowering of symmetry such as has been seen before in some forms of the zirconosilicate system [13].

Table 1. Atomic molar ratios normalised to Ge based on XRF results.

<i>Element</i>	0% Nb		10% Nb		20% Nb		30% Nb	
	As-made	Cs-exchanged	As-made	Cs-exchanged	As-made	Cs-exchanged	As-made	Cs-exchanged
<i>Ge</i>	1	1	1	1	1	1	1	1
<i>Cs</i>		0.02		0.29		0.37		0.63
<i>K</i>	0.60	0.55	0.62	0.38	0.65	0.32	0.68	0.25
<i>Zr</i>	0.50	0.46	0.39	0.37	0.35	0.33	0.32	0.30
<i>Nb</i>			0.04	0.04	0.08	0.08	0.12	0.11

Rietveld analysis of the X-ray diffraction patterns for the parent and 30% doped samples was done to investigate if it was possible to correlate structural changes with the improved ion exchange properties. As the analysis used laboratory X-ray data, reasonable constraints were applied including linking all isotropic thermal parameters for any element type to be the same and for the 30% doped sample fixing the Nb fraction at 0.3 and the total potassium content to 1.7. The individual fractional occupancies for the potassium sites were allowed to vary but they stayed identical within error. Distance restraints for Zr/Nb–O of 2.07(5) Å and Ge–O of 1.74(5) Å were used. The final fit for the parent material had wR_p of 6.2% and χ^2 of 6.75 for 76 variables and that for the 30% material had wR_p of 3.9% and χ^2 of 3.06 for 88 variables, figure 3.

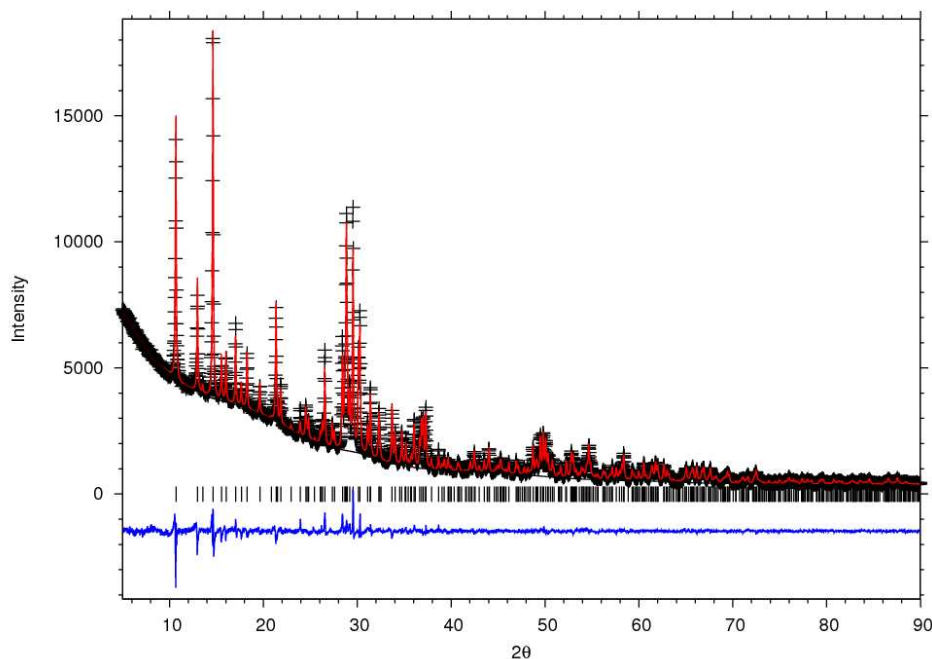


Figure 3. Rietveld refinement of the powder X-ray diffraction pattern of $K_{1.7}Zr_{0.7}Nb_{0.3}Ge_3O_9 \cdot H_2O$ with observed (crosses), calculated (top line) and difference (bottom line) plots and reflection markers.

The refined unit cell parameters are given in table 2. Although statistically significant differences were observed, the percentage changes are very small. The ionic radii for Zr^{4+} and Nb^{5+} in octahedral environments are 0.72 and 0.64 Å, respectively [14], so a small decrease in unit cell volume might be expected. The largest observed change is indeed a decrease in the b -axis, but the unit cell volume is not significantly changed. The locations and binding of the K^+ ions within the pores is also virtually unchanged. Overall, the only significant difference from the Nb-doping is a decrease in the occupancy of the two K^+ sites. We propose, therefore, that this is the underlying cause leading to an enhanced ion exchange of Cs^+ for K^+ in these umbite materials. The presence of cation defect sites within the tunnels would allow for greater mobility of cations. Finally we note that for the zirconosilicate analogue, ion exchange begins with K^+ exchanging for H^+ of water, again disrupting the regularity of cation binding inside the pores and enhancing the cation mobility [15].

Table 2. Selected refined crystallographic parameters from the Rietveld refinements of $K_{2-x}Zr_{1-x}Nb_xGe_3O_9 \cdot H_2O$. for $x = 0$ and 0.3.

	Parent	30% Nb	% change
$a / \text{Å}$	10.3661(2)	10.3764(2)	0.099
$b / \text{Å}$	13.6234(2)	13.5961(3)	-0.200
$c / \text{Å}$	7.4104(2)	7.4228(1)	0.167
$V / \text{Å}^3$	1046.50(5)	1047.19(4)	0.066
K1-O mean / Å	2.83	2.80	-1.06
K2-O mean / Å	2.87	2.89	0.70

CONCLUSIONS

Nb-doped zirconogermanates of general formula $K_{2-x}Zr_{1-x}Nb_xGe_3O_9 \cdot H_2O$ can be prepared as single phase materials up to $x \approx 0.30$. Although the undoped material shows poor ion exchange behavior towards Cs^+ , even 10% doping of Nb^{5+} for Zr^{4+} drastically improves the exchange and the amount of replacement of Cs for K increases with Nb content. From Rietveld analysis of powder X-ray diffraction data we attribute this to the creation of cation vacancies in the pores and a subsequent increase in ion mobility rather than any significant changes in the size or shape of the pore or bonding of the K^+ to the pore and water oxygen atoms.

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