Crystal Structure of $(R_{2-x}Ca_x)Zr_2O_{7-0.5x}$ (R = Nd, Gd) Compounds

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Two series of $(R_{2-x}Ca_x)Zr_2O_{7-0.5x}$ (R = Nd, Gd) compounds with disordered pyrochlore structure and a space group of Fd3m were prepared by a polymeric citrate precursor method. Single phase structure was found in a solubility range of $0 \le x \le 0.10$ for all compounds. Fig. 1 shows the XRD patterns of $(Gd_{2-x}Ca_x)Zr_2O_{7-0.5x}$ compounds. Unit cell parameters, bond distances and bond angles of the samples are listed in Table 1. Nd^{3+} and Ca^{2+} ions have similar ionic radius so that variation of the unit cell *a*-axis is small, in the range of $10.662 \le a \le 10.670$ Å. Increasing the amount of Ca ion, *x*-fractional coordinate of O(2) site and occupancy of O(3) are increased, but they were decreased above 0.075. Fig. 2 shows the Rietveld refinement result of the $Nd_{1.9}Ca_{0.1}Zr_2O_{6.95}$ compound. Fig. 3 shows the Zr *K*-edge XANES spectra of $(R_{2-x}Ca_x)Zr_2O_{7-0.5x}$ (R = Nd, Gd) compounds. Zr *K*-edge XANES spectra show that all the samples have Zr ions close to 4+ valence state.

Table1. Unit cell parameters of $(Nd_{2-x}Ca_x)Zr_2O_{7-0.5x}$

x	0	0.050	0.075	0.100
a (Å)	10.67039(2)	10.66672(7)	10.66255(1)	10.66679(7)
x-coordinate of O(2)	0.33620(3)	0.33659(7)	0.33684(6)	0.336448(1)
*g*O(3)	0.219(3)	0.227(2)	0.246(7)	0.2073(6)
R_{wp}	9.78(1)	9.35(2)	9.58(4)	9.24(3)
Nd–O(1) (Å) Zr–O(3) (Å)	2.31021(6)	2.30941(1)	2.30851(0)	2.30943(0)
Nd–O(2) (Å)	2.5715(2)	2.5679(3)	2.5650(4)	2.566(2)
Zr–O(2) (Å)	2.0986(1)	2.0996(2)	2.1001(3)	2.101(1)

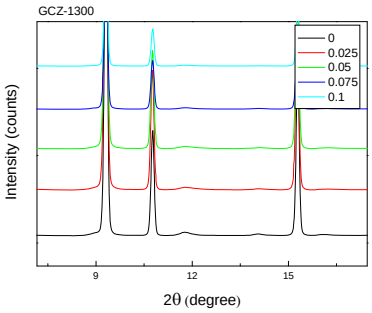

Figure 1. XRD patterns of $(Gd_{2-x}Ca_x)Zr_2O_{7-0.5x}$ compounds.

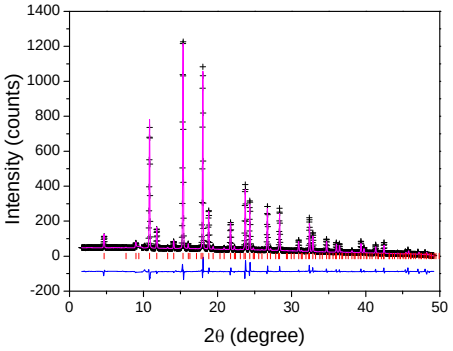

Figure 2. Rietveld refinement result of the $(Nd_{1.9}Ca_{0.1})Zr_2O_{6.95}$ compounds.

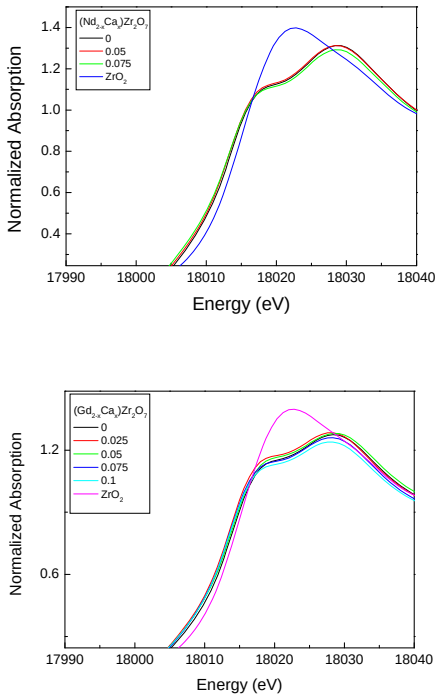

Figure 3. XANES spectra of Zr *K*-edge on the $(R_{2-x}Ca_x)Zr_2O_{7-0.5x}$ (R = Nd, Gd) compounds.