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Phase equilibria of $CaTiO_3$ doped with Ce, Nd and U

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Abstract

The solubility limits of Ce, Nd and U in $CaTiO_3$, one of the promising host matrix for fixation of lanthanide and actinide elements, were determined by X-ray diffraction to be between 20 and 30 mol%, between 20 and 30 mol% and between 0 and 3 mol%, respectively. By substituting Al to Ti in $CaTiO_3$, the solubility limit of U in $CaTiO_3$ increased to be between 5 and 7.5 mol%. The thermogravimetric analyses of $(Ca_{0.80}Ce_{0.20})TiO_{3\pm y}$ was carried out at 1273 K and 1373 K in the oxygen partial pressure range of 10^{-14}–10^{-6} Pa. In the higher oxygen partial pressure region, the sample of single $CaTiO_3$ phase decomposed into three phases consisting of perovskite phase, CeO_2 and TiO_2. © 1997 Elsevier Science B.V.

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1. Introduction

Perovskite phase $CaTiO_3$ has been recognized as one of the promising phase for immobilization of high level radioactive wastes [1,2], since this ceramic oxide can form solid solutions with lanthanides and actinides. Hence the studies on the phase equilibria of $CaTiO_3$ doped with lanthanides and actinides are important to understand the stabilities of waste forms at high temperatures which will be encountered in the preparation of these waste forms as well as storage of the waste.

From the close ionic radius of lanthanides to that of calcium ion, lanthanides has been reported to substitute for calcium, keeping the electrical neutrality by reduction of titanium ion from tetravalence to trivalence [3]. On the other hand, Larson et al. [4] have reported that electrical neutrality condition in $(Ca_{0.925}Gd_{0.075})TiO_3$ was kept by the presence of cation vacancy from the results of EPR, EXAFS and Raman spectroscopic analyses. Rossow et al. [5] have reported that tetravalent uranium occupied the calcium site and that solubility limit of uranium was about 5 mol% by EDX analysis. Evans et al. [6] reported that plutonium could be soluble as the form of $(Ca_{0.96}Pu_{0.04})TiO_3$.

In the present study, the solubility limits of Ce, Nd and U in $CaTiO_3$ were determined by X-ray diffraction, where cerium and neodymium were chosen to simulate the behavior of transuranium elements (TRU). The thermogravimetric studies on $(Ca_{0.80}Ce_{0.20})TiO_3$ were also carried out in the oxygen partial pressure range of 10^{-14} to 10^{-6} Pa at 1273 K and 1373 K to clarify the oxygen non-stoichiometry.

2. Experimental

Powders of 99.99% pure $CaCO_3$, TiO_2, CeO_2, Nd_2O_3, UO_2 and Al_2O_3 were used for the preparation of the solid solution samples. These powders were weighted and mixed so as to be stoichiometric composition, then pressed into pellets under a pressure of 400 kg/cm^2. The samples doped with Ce and U were heated at 1600 K in purified argon for about 100 h. Neodymium doped samples were heated at 1600 K in air for about 100 h. The formation of single phase solid solution was investigated by X-ray diffraction.

The thermogravimetric studies were carried out with a CARN RG microbalance. The various oxygen partial pressures were obtained by regulating the mixing ratio of CO_2/H_2 gases. The buoyancy of the sample was corrected by using Pt wires of the same weight as the sample placed in crucible inside a glass tubing. The peak-to-peak noise of the thermobalance was about 10 μg, due mainly to gas turbulence. The thermogravimetric analyses of $(Ca_{0.80}Ce_{0.20})TiO_3$ were carried out at 1273 K and 1373 K

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in the oxygen partial pressure of 10^{-14} Pa to 10^{-6} Pa. The oxygen partial pressure was determined by CoO and TiO_2 monitor calibrated in our laboratory.

3. Results and discussion

3.1. The solubility limits

3.1.1. Cerium doped $CaTiO_3$

For cerium doped samples, single phase could not be formed by heating them in air and also in argon, where the oxygen partial pressure is about 2.0 Pa. Hence single phase sample was prepared in an argon gas purified with titanium getter, of which oxygen partial pressure was determined to be about 1×10^{-10} Pa. The lattice parameters obtained for Ce-doped samples, thus prepared, in this study are shown in Fig. 1. It is seen in the figure that the lattice parameters, *a*, *b* and *c* do not show the monotonical change with increasing Ce content, probably due to the change in the oxygen non-stoichiometry and valence of Ti to keep the electroneutrality condition with increasing Ce content. The appearance of the other phases in addition to the perovskite phase was observed at 30 mol% Ce by X-ray diffraction. The other phases were identified to be CeO_2 and TiO_2. Considering the appearance of the second and third phases, the solubility limit of Ce in $CaTiO_3$ was concluded to be between 20 and 30 mol%.

3.1.2. Neodynium doped $CaTiO_3$

The lattice parameters, *a*, *b* and *c* for Nd-doped samples obtained in this study are shown in Fig. 2 as a function of mol% Nd. It is seen in the figure that compositional dependences of lattice parameters, *a*, *b* and *c* in neodynium doped $CaTiO_3$ are not simple. As neodynium concentration exceeded 30 mol%, the second phase, $Nd_2Ti_2O_7$, was identified. Considering the appearance of the second phase, the solubility limit of Nd in $CaTiO_3$ was determined to be between 20 and 30 mol%.

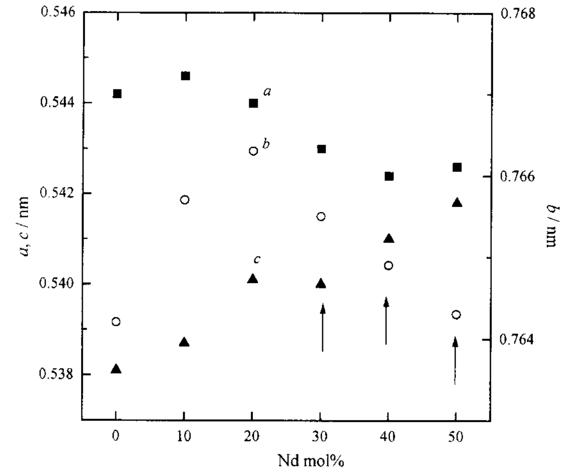

Fig. 2. Lattice parameters of $CaTiO_3$ doped with Nd. Arrows show the presence of two-phase mixture. ■, *a*; □, *b*; ▲, *c*.

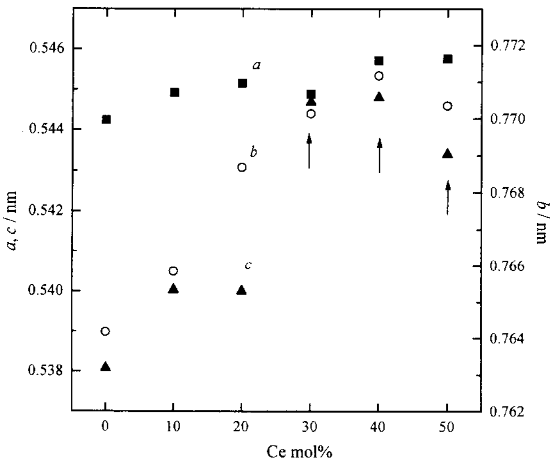

Fig. 1. Lattice parameters of $CaTiO_3$ doped with Ce. Arrows show the presence of three-phase mixture. ■, *a*; □, *b*; ▲, *c*.

3.1.3. Uranium doped $CaTiO_3$

The lattice parameters, *a*, *b* and *c* for U-doped samples are shown in Fig. 3 as a function of mol% U. As seen in the figure, the lattice parameters *a* and *c* do not change so much with increasing U content. Single perovskite phase could not be obtained even by doping 3 mol% U in $CaTiO_3$, probably due to the tetravalency of U differently from the trivalency of Ce and Nd substituted for divalent Ca in $CaTiO_3$. As the second phase, $CaUO_4$ was identified from the X-ray diffraction pattern. To make easy the achievement of the electroneutrality condition in the case of U-doping, the trivalent Al was doped into $CaTiO_3$ by twice amount of U so as to substitute to tetravalent Ti. The lattice parameters *a*, *b* and *c* of $(Ca_{1-x}U_x)(Ti_{1-2x}Al_{2x})O_3$ are shown in Fig. 4 as a function of U content. Compared

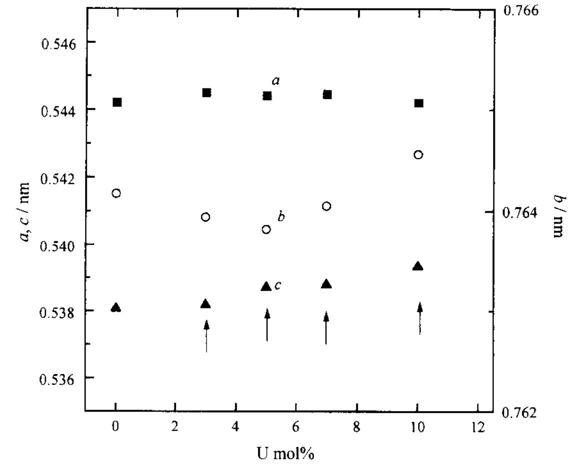

Fig. 3. Lattice parameters of $CaTiO_3$ doped with U. Arrows show the presence of two-phase mixture. ■, *a*; □, *b*; ▲, *c*.

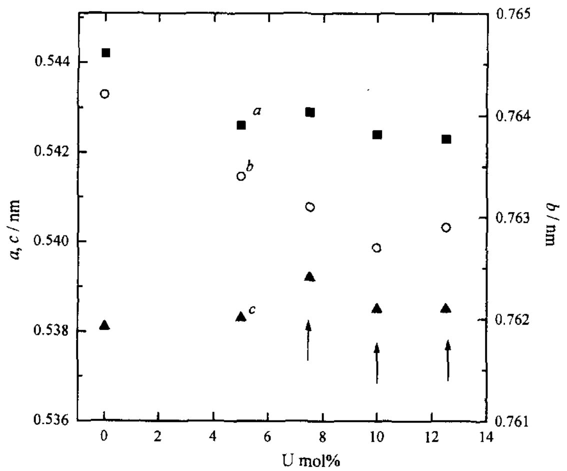

Fig. 4. Lattice parameters of Ca(Ti, Al)O_3 doped with U. Arrows show the presence of two-phase mixture. ■, *a*; □, *b*; ▲, *c*.

to the result in Fig. 3, the solubility limit of uranium at calcium site increased to be between 5 and 7.5 mol%. Second phase appeared above the compositions 7.5 mol% U in $(Ca_{1-x}U_x)(Ti_{1-2x}Al_{2x})O_3$ was identified to be $CaUO_4$.

3.2. Oxygen non-stoichiometry

The weight changes of $(Ca_{0.80}Ce_{0.20})TiO_{3\pm y}$ measured by thermogravimetry at 1273 K and 1373 K are shown in Figs. 5 and 6, respectively. It is seen in these figures that a single phase $(Ca_{0.80}Ce_{0.20})TiO_3$ decomposes into a mixed phase in higher oxygen partial pressures regions, i.e., above 2×10^{-12} Pa and 2×10^{-11} Pa, at 1273 K and 1373 K, respectively. The presence of the mixed phases at both 1273 and 1373 K at and above 2×10^{-12} Pa and 2×10^{-11} Pa, respectively, was also confirmed by X-ray diffraction and the mixed phases were identified to be composed of perovskite, cerium dioxide and titanium dioxide. Trivalent cerium ion was thought to be stable in low oxygen partial pressure. In higher oxygen partial pressure, tetravalent cerium ion may be more stable than trivalent one, producing cerium dioxide as one of the decomposed phases. The value of nonstoichiometry y in $(Ca_{0.80}Ce_{0.20})TiO_{3\pm y}$ could not be calculated since the value y at the phase boundary could not be definitely determined at moment.

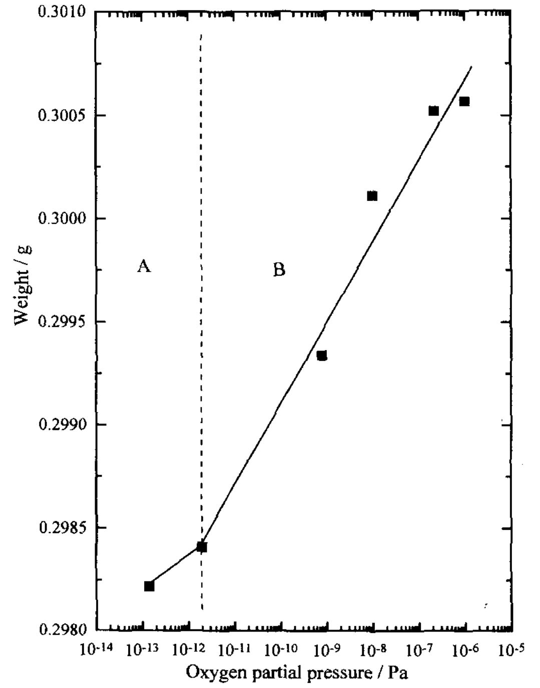

Fig. 5. Weight change of $(Ca_{0.80}Ce_{0.20})TiO_{3\pm y}$ at 1273 K. (A) a single-phase region of perovskite, (B) mixed-phase region of perovskite, CeO_2 and TiO_2.

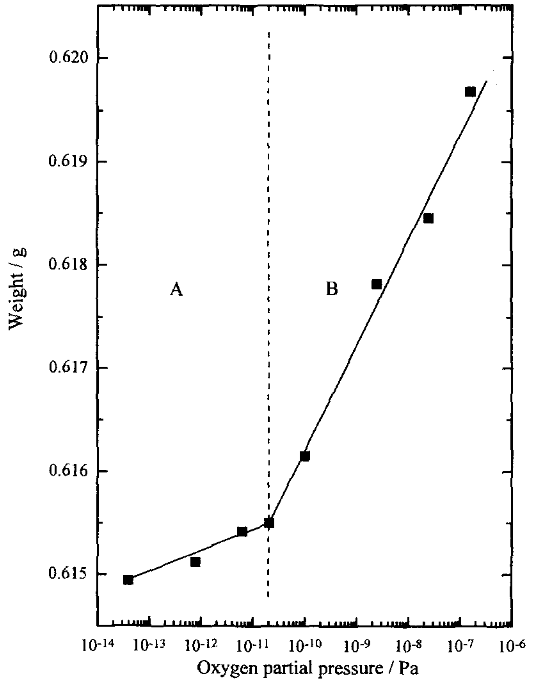

Fig. 6. Weight change of $(Ca_{0.80}Ce_{0.20})TiO_{3\pm y}$ at 1373 K. (A) a single-phase region of perovskite, (B) mixed-phase region of perovskite, CeO_2 and TiO_2.

4. Conclusions

The solubility limits of Ce, Nd and U in $CaTiO_3$ were found to be between 20 and 30 mol%, between 20 and 30 mol% and between 0 and 3 mol%, respectively. In the case of $(Ca_{1-x}U_x)(Ti_{1-2x}Al_{2x})O_3$, solubility limit of uranium increased up to be between 5 and 7.5 mol%. The compositional dependences of the lattice parameters *a*, *b* and *c* for all cases did not show the monotonical change with dopant content, probably due to the change in the oxygen non-stoichiometry and valence of titanium to keep the electroneutrality condition with increasing Ce content. As the decomposed phases in addition to the perovskite phase, CeO_2, TiO_2, $Nd_2Ti_2O_7$ and $CaUO_4$ were observed in the compositional range above solid solubility limits. Single phase $(Ca_{0.80}Ce_{0.20})TiO_{3\pm y}$ was unstable above the oxygen pressures of 2×10^{-12} Pa and 2×10^{-11} Pa at 1273 K and 1373 K, respectively.

Acknowledgements

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References

[1] G.J. McCarthy, Nucl. Technol. 32 (1977) 92.
[2] R. Roy, Radioact. Waste Disposal 1 (1982) 36.
[3] G.R. Lumpkin, K.L. Smith, M.G. Blackford, J. Nucl. Mater. 224 (1995) 131.
[4] E.M. Larson, P.G. Eller, J.D. Purzon, C.F. Pace, J. Solid State Chem. 73 (1988) 480.
[5] B.C.J. Rossow, P.S. Turner, T.J. White, Philos. Mag. B57 (1988) 227.
[6] J.P. Evans, J.A.C. Marples, Rep. No. AERE-G3592 Atomic Energy Research Establishment Harwell, Didcot, Oxfordshire, UK, 1985.