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Heat capacity measurements on $CaTiO_3$ doped with Ce and La

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Abstract

Heat capacity measurements were carried out on $(Ca_{0.85}Ce_{0.15})TiO_3$ and $(Ca_{0.85}La_{0.15})TiO_3$ in the temperature range of 292–1550 K by using a direct heating pulse calorimeter. The results indicate the presence of two phase transitions, one at 1380 ± 20 K and another at 1540 ± 20 K in $(Ca_{0.85}Ce_{0.15})TiO_3$ and one at 1380 ± 20 K and another above 1500 K in $(Ca_{0.85}La_{0.15})TiO_3$. The kind of dopant appeared to have no obvious difference on the transition temperature. The measured heat capacity data were used to derive the values of the thermodynamic functions, namely enthalpy increment, entropy and free energy function, as a function of temperature. The enthalpy and the entropy of the phase transitions were calculated from the heat capacity change. © 1997 Elsevier Science B.V.

1. Introduction

As the waste forms for the disposal of high level radioactive wastes, multi-phase crystalline ceramics which are natural mineral analogues have been developed [1,2]. In these ceramics, $CaTiO_3$ with the perovskite structure is one of the important constituents and can solve substitutionary the lanthanides and the actinides in the waste [3]. Hence thermodynamic properties of the solid solutions of $CaTiO_3$ with lanthanides and actinides are thought to be important to understand the stabilities of the waste forms at the temperatures which will be encountered in the fabrication of these waste forms as well as storage of the waste. Thermodynamic investigations on undoped $CaTiO_3$ reported in the literature are limited [4–6] and there is also a considerable difference in the transition temperature, the transition enthalpies and the crystallographic change of undoped $CaTiO_3$ in the previous reports [5,6]. Concerning doped $CaTiO_3$, the heat capacity of Nd-doped $CaTiO_3$ has been recently measured in our laboratory [7] and the presence of two phase transitions, one at 1386 K and another at 1528 K, has been found at a very close temperature to those of undoped $CaTiO_3$.

In this study, among lanthanide elements, Ce was chosen to simulate the behavior of its transuranium (TRU) counterpart and La was itself a main constituent of the fission-products. The heat capacity measurements were carried out on $CaTiO_3$ doped with 15 mol% of Ce and La in the temperature range of 292–1550 K by using a direct heating pulse calorimeter. The measured heat capacity data were used to derive the values of the thermodynamic functions, namely enthalpy increment, entropy and free energy function, as a function of temperature.

2. Experimental

Powders of $CaCO_3$, TiO_2, CeO_2 and La_2O_3 with 99.99% in purity supplied by Rare Metallic Co., Tokyo were used for the preparation of the solid solution samples. The cylindrical rods of about 4–6 mm in diameter and about 50–60 mm in length were fabricated for the heat capacity measurements by pressing the powder mixture containing stoichiometric amounts of the component oxide in a latex rubber tube under a hydrostatic pressure of 40 MPa. The rods were then heated at 1600 K under a purified argon atmosphere for about 170 h. The formation of single-phase solid solutions was confirmed by X-ray diffraction. Heat capacity measurements were carried out on $(Ca_{0.85}Ce_{0.15})TiO_3$ and $(Ca_{0.85}La_{0.15})TiO_3$ in the temperature range 292–1550 K by using a direct heating pulse

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calorimeter which has been described elsewhere [8]. In this calorimeter, the sample in the form of a rod and a molybdenum thermal shield maintained at a constant temperature in a platinum furnace are simultaneously heated by electric pulses such that the temperature increments of both the sample and the shield are equal, thus maintaining the adiabatic condition. The heat capacity of the sample is then calculated from the amount of electrical energy supplied to the sample and the measured increase in the sample temperature.

3. Results and discussion

3.1. Heat capacity

The heat capacity values of $(Ca_{0.85}Ce_{0.15})TiO_3$ in the temperature range 292–1550 K are shown as a function of temperature in Fig. 1. The error in the pulse calorimetric measurements has been determined to be ±2% in the earlier measurements on UO_2 [9]. The present data of the heat capacity of $(Ca_{0.85}Ce_{0.15})TiO_3$ are consistent with the values estimated using the additivity law from the heat capacity of $CaTiO_3$ and CeO_2 below 1276 K. The polynomial expression in temperature obtained by the least squares fitting of the data in the temperature range of 292–1276 K is given by the following equation:

$$\left(C_p/\mathrm{J\ mol^{-1}\ K^{-1}}\right) = 115.7899 + 9.6617 \times 10^{-3}\ (T/\mathrm{K}) - 1.94366 \times 10^{6}\ (\mathrm{K}/T)^2. \quad (1)$$

The heat capacity values computed by using the above equation are shown in Fig. 1 as a solid line. These heat capacity values as well as the values for the enthalpy increment, entropy and free energy function derived from the above equation are given in Table 1. The S^0_{298} value required for the above computations was estimated from the literature data of S^0_{298} values for $CaTiO_3$ and CeO_2 by using the additivity law as a first approximation.

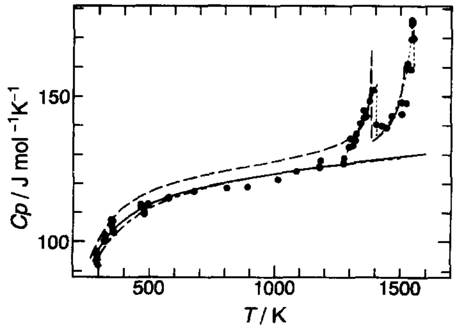

Fig. 1. Heat capacity of $(Ca_{0.85}Ce_{0.15})TiO_3$. (●) Measured values; (————) least square fitted curve; (---) undoped $CaTiO_3$ [6] and (– · –) heat capacity calculated by additivity law.

The heat capacity values of $(Ca_{0.85}La_{0.15})TiO_3$ in the temperature range 302–1504 K are shown in Fig. 2 as a function of temperature. The present data of the heat capacity below 1224 K are between the values estimated using the additivity law from the heat capacity of $CaTiO_3$ and La_2O_3 and the value of undoped $CaTiO_3$. The heat capacity data in the temperature range of 302–1224 K were fitted by the least squares method and the expression obtained is given by Eq. (2),

$$\left(C_p/\mathrm{J\ mol^{-1}\ K^{-1}}\right) = 117.2269 + 1.1104 \times 10^{-2}\ (T/\mathrm{K}) - 2.63846 \times 10^{6}\ (\mathrm{K}/T)^2, \quad (2)$$

which is shown as a solid line in Fig. 2. The values for the thermodynamic functions for $(Ca_{0.85}La_{0.15})TiO_3$ computed from the heat capacity values given by the above equation using S^0_{298} values for $CaTiO_3$ and La_2O_3 estimated similarly to the case of $(Ca_{0.85}Ce_{0.15})TiO_3$ are given in Table 2.

3.2. Phase transitions

The heat capacity values of $(Ca_{0.85}Ce_{0.15})TiO_3$ and $(Ca_{0.85}La_{0.15})TiO_3$ measured in the present study are shown in Figs. 1 and 2 in comparison with those of

Table 1
Thermodynamic functions of $(Ca_{0.85}Ce_{0.15})TiO_3$

Temperature (K)	C_p (J mol^{-1} K^{-1})	S^0_T (J mol^{-1} K^{-1})	$-(G^0_T - H^0_{298.15})/T$ (J mol^{-1} K^{-1})	$H^0_T - H^0_{298.15}$ (kJ mol^{-1})
300	91.24	71.10	71.11	0.168
400	105.18	99.53	99.50	10.08
500	112.23	123.83	123.79	20.98
600	116.56	144.70	144.65	32.44
700	119.62	162.91	162.85	44.25
800	121.99	179.04	178.97	56.34
900	123.96	193.53	193.45	68.64
1000	125.69	206.68	206.60	81.12
1100	127.26	218.73	218.65	93.77
1200	128.72	229.87	229.78	106.57

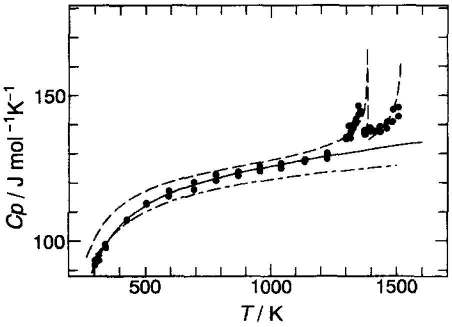

Fig. 2. Heat capacity of $(Ca_{0.85}La_{0.15})TiO_3$. (●) Measured values; (———) least square fitted curve; (- - -) undoped $CaTiO_3$ [6] and (– · –) heat capacity calculated by additivity law.

undoped $CaTiO_3$ by Guyot et al. [6], all of which show the presence of two phase transitions. The first transition for both $(Ca_{0.85}Ce_{0.15})TiO_3$ and $(Ca_{0.85}La_{0.15})TiO_3$ is seen to be at 1380 ± 20 K, which is close to the transition temperature 1384 K for undoped $CaTiO_3$ reported by Guyot et al. [6] and 1386 K for Nd doped $CaTiO_3$ recently found by heat capacity measurement in our laboratory [7]. According to the recent result by high temperature X-ray diffraction for undoped and Nd-doped $CaTiO_3$ in our laboratory [10], the crystal structure was found to change from orthorhombic Pbnm to orthorhombic Cmcm near 1386 K. Since the doping to $CaTiO_3$ does not appear to have large influence on the transition temperature, it can be inferred that, in going from orthorhombic Pbnm to orthorhombic Cmcm at the first transition point, both the change in the interoctahedral rotation about one of the axes of the TiO_6 octahedra and the displacement of the calcium atoms surrounded by the eight TiO_6 octahedra are small. The difference between the ionic radii of calcium and dopant atoms (0.134 nm for Ca^{2+}, 0.127 nm for Nd^{3+}, 0.134 nm for Ce^{3+} and 0.136 nm for La^{3+} [11]) is not very large and hence the result is not surprising.

The heat capacity values of $(Ca_{0.85}Ce_{0.15})TiO_3$ shown in Fig. 1 also indicate the presence of the second phase transition around 1540 ± 20 K which is also close to 1528 K obtained for $(Ca_{0.85}Nd_{0.15})TiO_3$ [7]. Although the presence of the second transition could not be clearly confirmed from the heat capacity measurement in the case of $(Ca_{0.85}La_{0.15})TiO_3$ due to considerable noise in the thermocouple signal used for temperature measurement above 1505 K, the presence of the second transition around 1540 ± 20 K is expected, since the transition mechanism of the first and the second transitions is very similar to each other according to the results by X-ray diffraction [6,10,12] and the transition temperatures for the first transition for both $(Ca_{0.85}Ce_{0.15})TiO_3$ and $(Ca_{0.85}La_{0.15})TiO_3$ observed in this study and $(Ca_{0.85}Nd_{0.15})TiO_3$ [7] are not so different. The enthalpy and the entropy of the first transition were calculated from our heat capacity measurements of $(Ca_{0.85}Ce_{0.15})TiO_3$ to be 1.4 ± 0.4 kJ mol^{-1} and 1.0 ± 0.3 J mol^{-1} K^{-1}, respectively. The enthalpy of transition for $(Ca_{0.85}Ce_{0.15})TiO_3$ is not so different from 1.8 ± 0.4 kJ mol^{-1} for $(Ca_{0.85}Nd_{0.15})TiO_3$ [7] and 1.0 ± 0.4 kJ mol^{-1} of Guyot et al. [6] considering the large error in all measurements. Since the transition temperatures for the doped and the undoped $CaTiO_3$ are not very different, the enthalpy of the phase transition is also not expected to be very different. The present data of the enthalpy of transition for $(Ca_{0.85}Ce_{0.15})TiO_3$ directly measured from the heat capacity data could be more reliable than those calculated by Guyot et al. [6] from the heat capacities derived from the enthalpy increment data by drop calorimetry. Due to lack of the data point around the exact first transition point, the enthalpy of the phase transition in $(Ca_{0.85}La_{0.15})TiO_3$ could not be determined.

4. Conclusion

There were two phase transitions in $(Ca_{0.85}Ce_{0.15})TiO_3$, one at 1380 ± 20 K and another at 1540 ± 20 K as was reported for undoped $CaTiO_3$ [6]. There also seemed to be two phase transitions in $(Ca_{0.85}La_{0.15})TiO_3$, one at 1380 ±

Table 2
Thermodynamic functions of $(Ca_{0.85}La_{0.15})TiO_3$

Temperature (K)	C_p (J mol^{-1} K^{-1})	S_T° (J mol^{-1} K^{-1})	$-(G_T^\circ - H_{298.15}^\circ)/T$ (J mol^{-1} K^{-1})	$H_T^\circ - H_{298.15}^\circ$ (kJ mol^{-1})
300	91.33	75.98	75.98	0.169
400	105.08	104.40	104.38	10.08
500	112.16	128.71	128.66	20.97
600	116.55	149.58	149.52	32.42
700	119.65	167.79	167.72	44.24
800	122.04	183.92	183.85	56.33
900	124.01	198.40	198.33	68.63
1000	125.72	211.56	211.47	81.12
1100	127.26	223.61	223.52	93.77
1200	128.67	234.75	234.66	106.57

20 K and another above 1500 K. The doping of $CaTiO_3$ with Nd, Ce and La does not have much influence on the transition temperatures. The calculated values of the enthalpy and the entropy of the first transition for $(Ca_{0.85}Ce_{0.15})TiO_3$ are 1.4 ± 0.4 kJ mol^{-1} and 1.0 ± 0.3 J mol^{-1} K^{-1}, respectively.

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