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Thermal expansion of ZrP_2O_7 and related solid solutions

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The effect of solute ions on the thermal expansion of ZrP_2O_7 solid solutions was studied. The abrupt thermal expansion at the high–low inversion can be interpreted as due to the rotation of the polyhedra from the low-temperature form in the partially collapsed state to the high-temperature form in the fully expanded state. The replacement of zirconium ions by larger ions and/or the stuffing of cations into the cavities of the framework stabilized the expanded structure, and then depressed the abruptness of the expansion. Consequently the thermal expansion was reduced in $Ce_xZr_{1-x}P_2O_7$ or $(Li, Y)_xZr_{1-x}P_2O_7$ solid solutions.

1. Introduction

In the system ZrO_2–P_2O_5 there are two compounds with 2 : 1 and 1 : 1 ratios of ZrO_2 to P_2O_5. The former, $(ZrO)_2P_2O_7$, was investigated as a low thermal expansion ceramic [1, 2]. The latter, ZrP_2O_7, has a reversible inversion at about 300° C [1, 3]. The thermal expansion is similar to that of cristobalite, being rather low in the region above the inversion temperature. There is a 0.6% difference in volume between high and low temperature forms of ZrP_2O_7. The ceramics are stressed by this abrupt expansion or contraction during temperature cycling, resulting in mechanical failure. In order to obtain stabilized ceramics it is necessary to remove the inversion.

Laud *et al.* [4] reported that a low-expansive solid solution of high-temperature form was obtained in the region of the low-temperature form by a mutual stabilization process between the phases ZrP_2O_7 and ThP_2O_7. More detailed studies have not yet been conducted. In addition, beta-eucryptite ($LiAlSiO_4$) is derived from low-thermal-expansive high-quartz, in which Al^{3+} ions replace Si^{4+} ions and Li^+ ions are stuffed into interstices in the structure in order to maintain a charge balance. In this study, therefore, various solid solutions of ZrP_2O_7 were examined in order to stabilize the high-temperature form.

2. Experimental procedure

Chemicals of reagent grade were used in the preparations. The desired compositions of ZrP_2O_7 solid solution were prepared by direct mixing of a concentrated solution of phosphoric acid, zirconium oxychloride and substituting metal chloride, oxide, or carbonate in a mortar. The resultant suspension was evaporated to dryness, and calcined at 600° C. The calcined materials were ground, pressed to form a tablet and then fired at temperatures ranging from 1200 to 1500° C.

The products were identified and the lattice parameters were measured by X-ray powder diffraction. The thermal expansion of polycrystalline ceramics was measured with a fused-silica dilatometer at a heating rate of $10° C\,min^{-1}$ from room temperature to 800° C. The thermal expansion of the unit cell was also determined with a high-temperature X-ray diffractometer. Procedures for measurement and data processing have been described previously in detail [5]. The presence of the inversion was also confirmed by differential thermal analysis.

3. Results

The pyrophosphates of silicon, titanium, tin, lead, cerium, thallium, uranium and zirconium form a series of isostructural cubic crystals [6–8]. Therefore, the solid solutions between ZrP_2O_7 and some members of this family were first investigated.

Figs 1 and 2 show typical DTA and thermal expansion curves of the solid solutions obtained, in which the tin and cerium solid solutions contained minor phases other than MP_2O_7. When Zr^{4+} ions were

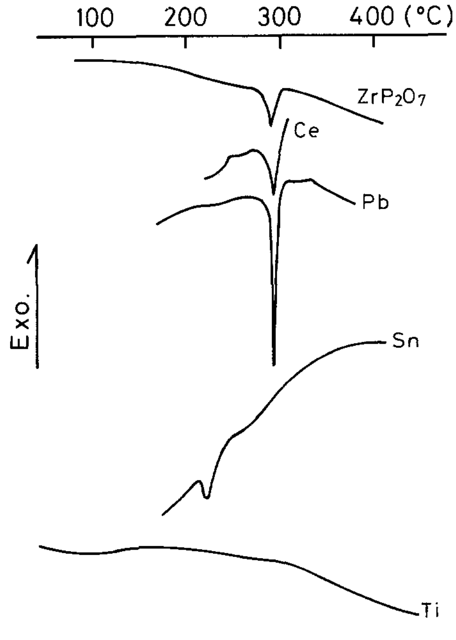

Figure 1 DTA curves of $M_{0.2}Zr_{0.8}P_2O_7$ solid solutions (M = metal).

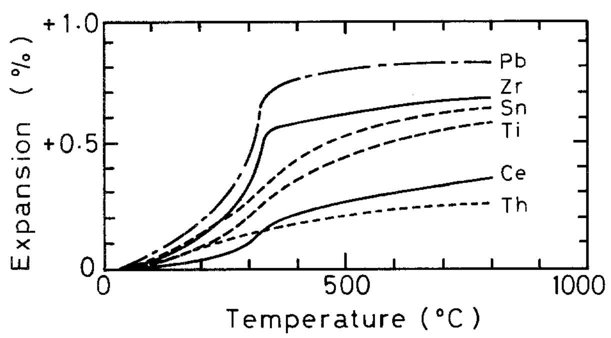

Figure 2 Thermal expansion curves of polycrystalline $M_{0.2}Zr_{0.8}P_2O_7$ solid solutions (M = metal).

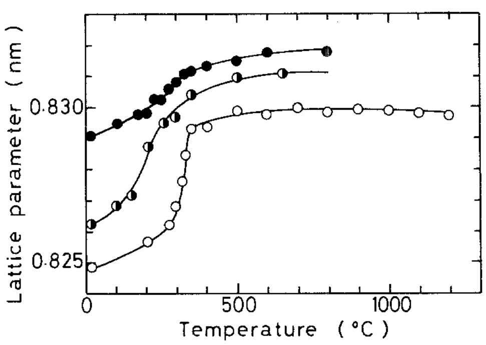

Figure 3 Crystal lattice thermal expansion of $(Li, Y)_xZr_{1-x}P_2O_7$ solid solutions: x = (○) 0, (◑) 0.1, (●) 0.2.

replaced by small ions (Sn^{4+} or Ti^{4+}), the inversion points were shifted to lower temperature or faded, and their abrupt expansions due to inversion were relaxed. However the thermal expansions were still large (about $7 \times 10^{-6} (°C)^{-1}$). Both lattice parameters decreased compared with those expected from ionic radii. When Zr^{4+} ions were replaced by large ions (Ce^{4+} or Pb^{4+}), the inversion points hardly changed. Moreover the lead solid solution showed a rather too obvious inversion. The difference between high and low temperature forms decreased in the case of the cerium solid solution as well as the thallium solid solution [4]. The lattice parameter of the cerium solid solution slightly increased, while that of the lead solid solution slightly decreased.

The replacement of zirconium by a lithium and yttrium pair was then performed. The lattice parameter of $(Li, Y)_xZr_{1-x}P_2O_7$ solid solutions increased with increasing x and reached a maximum at the composition $x \fallingdotseq 0.2$, which was the limit of solid solution. The DTA curves did not exhibit any peaks. Fig. 3 shows the thermal expansion curves. The abrupt inversion was relaxed step by step with the replacement of zirconium by the lithium and yttrium pair. The average linear thermal expansion coefficient of $(Li, Y)_{0.2}Zr_{0.8}P_2O_7$ was about $4 \times 10^{-6} (°C)^{-1}$.

4. Discussion

The thermal expansion of a three-dimensional framework is the sum of a bond-length expansion and a tilting effect between polyhedra linked by their corners [9]. When the polyhedra are tilted away from symmetrical orientations, tilting effects are generally larger, and a change of tilt angle often culminates in a phase inversion. For example, the abrupt expansion of quartz up to the inversion temperature is due to the rotation of the tetrahedra from the partially collapsed state to the fully expanded state [10].

As the structure of ZrP_2O_7 is linked only by the corners of ZrO_6 octahedra and PO_4 tetrahedra [8], a bond-angle change among polyhedra, i.e. tilting, becomes possible. Fig. 4 shows schematic diagrams for the partially collapsed (right) and fully expanded structures (left) of ZrP_2O_7. It is supposed that the low and high forms of ZrP_2O_7 correspond to the partially collapsed and fully expanded structure, respectively. Consequently, it is also concluded that the abrupt expansion of ZrP_2O_7 is due to the rotation of the ZrO_6 octahedra and PO_4 tetrahedra from the partially collapsed state to the fully expanded state.

The lattice parameter of ZrP_2O_7 is represented by the equation shown in Fig. 5, where interatomic distances and bond angles are based on the crystallographic data of Chaunac [3]. In the three-dimensionally fully expanded state by simple geometric rotation, the parameter a_T is calculated to be 0.828 nm. At high temperature, the parameter would be further affected by the thermal expansion of bond lengths and the change of distortion of the polyhedra. Therefore, it is thought that this a_T approximates to the actual value of the high-temperature form after inversion as shown in Fig. 3.

The replacement of Zr^{4+} ions by Ti^{4+}, Sn^{4+}, Pb^{4+} or Ce^{4+} ions should more or less change the tilting angle. When smaller SnO_6 or TiO_6 octahedra replace larger ZrO_6 octahedra, they would be almost stretched without tilts. Then the degree of total tilting would decrease and the expansion would relax. On the other hand it is considered that there are two ways of replacing by larger octahedra. In the case of the lead solid solution,

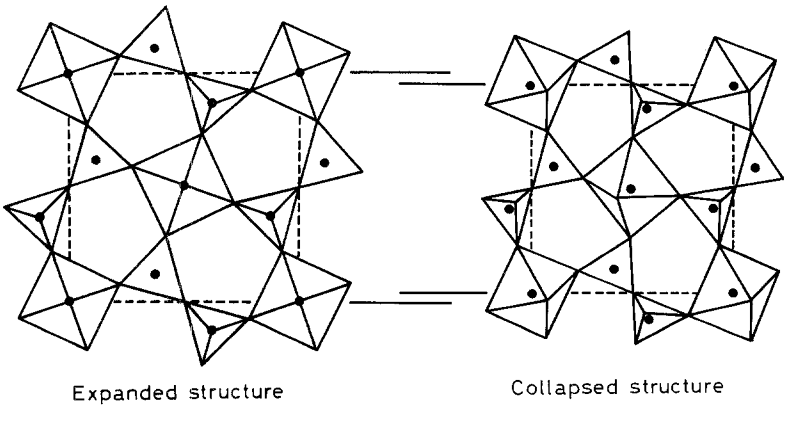

Figure 4 Schematic diagrams for the partially collapsed (right) and fully expanded structure (left) of ZrP_2O_7.

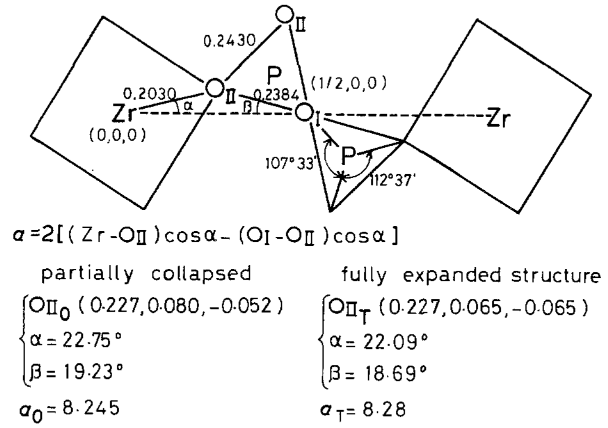

Figure 5 Lattice parameter of ZrP_2O_7 in a polyhedral representation. Bond lengths are in nanometres.

PbO_6 octahedra were more tilted than ZrO_6 octahedra, so it exhibited a remarkable inversion. In the cases of the cerium and thallium solid solutions the tilting ZrO_6 octahedra were stretched in accordance with the larger CeO_6 or ThO_6 octahedra, so the structure was close to the expanded state and the thermal expansion decreased. The difference between the lead and cerium or thallium solid solutions can be explained on the basis of electronegativity. The electronegativity of lead is larger than that of cerium or thallium, so that the Pb–O bond has a more covalent tendency than Ce–O or Th–O bonds. Consequently PbO_6 octahedra should be considerably distorted.

In addition, when the Zr^{4+} ions were replaced by Li^+ and Y^{3+} pairs, the Li^+ ions could be located in the cavities of the framework, and then the tilting ZrO_6 octahedra were stretched toward the expanded state by stuffing the cavity with cations. Consequently the thermal expansion became smaller.

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