Lattice thermal expansion of zircon-type LuPO₄ and LuVO₄: A comparative study

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ABSTRACT

We report the lattice thermal expansion of zircon-(xenotime-)type LuPO₄ and LuVO₄ in the temperature range of 25–1000 °C from high-temperature powder XRD studies. The details of the high-temperature crystal chemistry of both phases have been determined from Rietveld analysis of the powder XRD data. Both the compounds show appreciably higher thermal expansion than analogous zircon-type silicates. Despite isomorphism, the axial thermal expansion of LuVO₄ shows significant anisotropy compared to LuPO₄. In the studied temperature range, the average axial thermal expansion coefficients of LuPO₄ are \( \alpha_a = 6.0 \times 10^{-6} \) and \( \alpha_c = 7.2 \times 10^{-6} \) (°C) and those of LuVO₄ are \( \alpha_a = 3.6 \times 10^{-6} \) and \( \alpha_c = 11.8 \times 10^{-6} \) (°C). However, the average volume thermal expansion coefficients are almost identical. The differences in the thermal expansion behavior of the two structures originate from differences in the expansion and distortion of the LuO₈ polyhedra. The LuPO₄ polyhedron in LuVO₄ shows about 30% higher thermal expansion than that in LuPO₄. The overall thermal expansion behaviors of these two structures are predominantly related to the distortion in the LuO₈ unit, inter-cation distances and spatial arrangement of the Lu-O bonds in the structure.

Keywords: Thermal expansion, crystal chemistry, zircon, xenotime, phosphates, vanadates

INTRODUCTION

The ABO₄-type compounds have been of interest because of technologically important physical properties (Kaminskii 1990; Scott et al. 2002) as well as mineralogical importance in understanding their crystal chemistry (Knittle and Williams 1993). The diversity of crystal chemistry of ABO₄ compounds is controlled by the ionic radii and charge combination of the A and B cations (Carron et al. 1958; Aldred 1984; Depero and Sangaletti 1997; Muller and Roy 1974). Depending on the ionic radii and charge combination of the cations, these compounds crystallize in scheelite-, monazite-, zircon-, and wolframite-type structures. Among the ABO₄ compounds with A³⁺ and B⁵⁺ combinations, structures related to scheelite (I₄/m, a), monazite (P2₁/c), zircon (I₄/m, amd), MnSO₄ (Cmcm), CrPO₄ (Imma), and silica, are known either at ambient or non-ambient pressure-temperature conditions. However, with a rare earth, viz. La-Lu, Y, and Sc as one of the trivalent ions, the only crystal structures known for B = P and V cation are monazite- and zircon-type structures (Beall et al. 1981; Boattner 2002; Ni et al. 1995; Chakoumakos et al. 1994; Mullica et al. 1996). Almost all the heavier lanthanide phosphates and vanadates crystallize in zircon-type structures. The structural studies on these compounds under high pressure and/or high temperature revealed various displacive and reconstructive transformations in them (Errandonea et al. 2004; Jayaraman et al. 1985; Wang et al. 2004; Sen et al. 2003; Mittal et al. 2008).

The zircon-(xenotime-)type ABO₄ materials are known for their low thermal expansion and incompressible stable structure under moderate pressure. However, under significantly higher pressure, zircon and its analogs transform to scheelite and post-scheelite structures. Also, among the zircon-group materials the thermal expansion behaviors are drastically different depending upon the cation charge and ionic radii combination (Bayer 1972; Subbarao et al. 1990; Li et al. 2007; Taylor 1986). Although both phosphates and vanadates of rare-earth ions have similar structural arrangements of AO₄ (bisdisphenoid, A = trivalent rare-earth ion) and PO₄ or VO₄ tetrahedra (Ni et al. 1995; Chakoumakos et al. 1994; Mullica et al. 1996), the differences in thermophysical behaviors due to the tetrahedral groups are remarkable. To evaluate the effect of ionic radii on the thermal expansion of these materials, several high-temperature studies have been performed on rare-earth vanadates and phosphates (Bayer 1972; Subbarao et al. 1990; Li et al. 2007; Taylor 1986; N. Reddy et al. 1981; Reddy et al. 1985, 1988, 1995). A comparison of the thermal expansion behavior of various zircon-group compounds shows significantly more anisotropic expansion for vanadates than phosphates. In addition, among these zircon-type ABO₄ compounds, heavier rare-earth phosphates and vanadates show significant anisotropy (Bayer 1972; Subbarao et al. 1990; Li et al. 2007; Taylor 1986). However, the detailed variations of the crystal structure or role of the crystal structures responsible for this have not been explained. It is well known that the increase in the mean bond length due to increasing amplitude of vibration of the atoms with temperature is reflected in the expansion of the material. Often crystal structure provides an explanation for thermal expansion behavior of a material. There are several reports correlating thermal expansion behavior with structural arrangements available in the literature (Khan 1976; Evans et al. 1996;