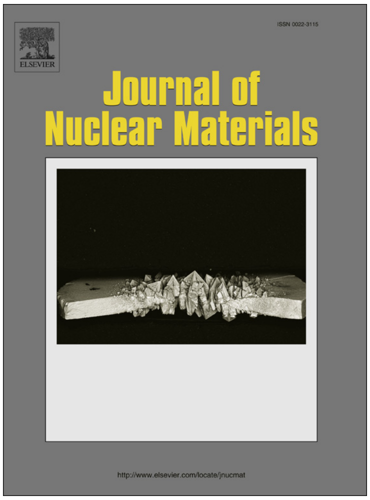
Heat capacities of lanthanide and actinide monazite-type ceramics

Piotr M. Kowalski, George Beridze, Victor Vinograd, Dirk Bosbach

PII: S0022-3115(15)00242-1
DOI: http://dx.doi.org/10.1016/j.jnucmat.2015.04.032
Reference: NUMA 49056

To appear in: *Journal of Nuclear Materials*

Received Date: 2 March 2015
Revised Date: 9 April 2015
Accepted Date: 13 April 2015



Please cite this article as: P.M. Kowalski, G. Beridze, V. Vinograd, D. Bosbach, Heat capacities of lanthanide and actinide monazite-type ceramics, *Journal of Nuclear Materials* (2015), doi: http://dx.doi.org/10.1016/j.jnucmat.2015.04.032

Heat capacities of lanthanide and actinide monazite-type ceramics

Piotr M. Kowalski[a,b,*], George Beridze[a,b], Victor Vinograd[a,b], Dirk Bosbach[a,b]

[a] *Institute of Energy and Climate Research (IEK-6), Forschungszentrum J¨*
[b] *JARA High-Performance Computing, Schinkelstraße 2, 52062 Aachen, Germany*

Abstract

$(Ln, An)_x PO_4$ monazite-type ceramics are considered as potential matrices for the disposal of nuclear waste. In this study we computed the heat capacities and the standard entropies of these compounds using density functional perturbation theory. The calculations of lanthanide monazites agree well with the existing experimental data and provide information on the variation of the standard heat capacities and entropies along the lanthanide series. The results for $AnPO_4$ monazites are similar to those obtained for the isoelectronic lanthanide compounds. This suggests that the missing thermodynamic data on actinide monazites could be similarly computed or assessed based on the properties of their lanthanide analogues. However, the computed heat capacity of $PuPO_4$ appear to be significantly lower than the measured data. We argue that this discrepancy might indicate potential problems with the existing experimental data or with their interpretation. This shows a need for further experimental studies of the heat capacities of actinide-bearing, monazite-type ceramics.

Keywords:
Ceramics, Ab initio calculations, Thermodynamics, Thermodynamic modeling, Nuclear Waste Management

---

1. Introduction

Radioactive waste is generated by a number of industrial processes, including electricity production. Direct disposal of spent nuclear fuel and vitrified high level waste in a deep geological repository is generally foreseen for the management of these wastes. Numerous studies on ceramic waste forms, including natural analogues, have demonstrated some of their advantageous properties as a matrix for immobilization of various radionuclides, in particular actinides. These include resistance to the radiation damage and stability when exposed to aqueous solutions [1, 2]. Monazite-type ceramics exhibit a number of properties relevant for the long-term isolation of actinides. Most importantly, their natural analogues preserve crystalline structure over geological times, in spite of being exposed to significant radiation doses [1, 3]. Before such a material can be utilized as a matrix for the disposal of nuclear waste, its thermodynamic properties must be well characterized. The heat capacity and entropy are important thermodynamic parameters useful for instance in the assessment of the thermodynamic stability of materials under repository condition. Although these thermodynamic functions have been measured for many lanthanide monazites, there exist only limited data on the actinide analogues [4, 5]. Dependence of the heat capacity and entropy on the physical and chemical properties of *Ln* and *An* cations is also poorly constrained [4].

The pure phase lanthanide and actinide monazite-type ceramics exist for *Ln*=La,...,Dy ($LnPO_4$) and *An*=Pu, Am, Cm ($AnPO_4$) [6]. The experimental data on the heat capacities and absolute entropies are available for some of these compounds. The low temperature heat capacities and the standard entropies have been measured for $LaPO_4$[7, 8, 9], $CePO_4$[10], $NdPO_4$[11], $EuPO_4$[12] and $GdPO_4$[8]. The high temperature heat capacities have been reported for $LaPO_4$[13], $CePO_4$[13], $NdPO_4$[11], $SmPO_4$[14], $EuPO_4$[14, 9] and $GdPO_4$[13]. For actinides, the analogous data are available only for $PuPO_4$ monazite. Thiriet et al. [4] and Benes et al. [15] measured the heat capacity of the pure $PuPO_4$ at low and high temperatures, respectively. Popa et al. [5] measured the low temperature heat capacity of the $La_{0.9}Pu_{0.1}PO_4$ solid solution.