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Plutonium in monazite and brabantite: Diffuse reflectance spectroscopy study

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Abstract

The valence states of plutonium (Pu) in monazite and brabantite have been studied by using diffuse reflectance spectroscopy. In the absence of charge compensators, Pu exists mainly as trivalent ions in air-fired monazites and only trivalent ions in argon-fired monazites. However, with added Ca^{2+}/Pb^{2+} as charge compensators Pu can exist as tetravalent ions. Published data on absorption spectra of both trivalent and tetravalent Pu ions in the monazite structure have been extended to the mid near infrared region (4000 cm^{-1}).
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1. Introduction

Monazite, a light rare-earth orthophosphate with general formula LnPO$_4$, has been proposed as an alternative waste form to confine radioactive wastes, including various types of reactor wastes and separated minor actinides, in its crystal lattice [1–4]. It has been observed to be chemically durable and radiation resistant in laboratory studies [5–7] both in the form of synthetic materials and natural minerals [8–10]. The early work on its structure, characteristics, preparation methods, chemical and physical properties, as well as chemical durability, as a waste form, has been extensively reviewed by Boatner and Sales [11]. In the late 1990s, monazite was also considered as a candidate phase for immobilisation of surplus impure Pu existing in the US and Russia. One advantage of a candidate ceramic phase for this purpose is its accommodation of neutron absorbers, and while the solubility of Gd in monazite is very high, this is not the case for Hf [12]. Also, its potential accommodation of impurity elements in the surplus Pu targeted for immobilisation was seen as very limited. However, in general terms, monazite is still a serious candidate for actinide immobilisation.

Monazite has a monoclinic structure (space group P2$_1$/n) [13] containing chains of alternating PO$_4$ tetrahedra and LnO$_9$ polyhedra (ninefold coordination with no symmetry elements other than the identity operator) which can incorporate trivalent and/or tetravalent elements [9,10,14]. Trivalent actinides (Ac^{3+}) can simply be incorporated by substitution of the Ln^{3+}, whereas tetravalent actinides (Ac^{4+}) can also be incorporated by the presence of bivalent cations (B^{2+}) as charge compensators forming an iso-structural compound with the general formula B$_x$Ac$_x$Ln$_{1-2x}$PO$_4$, also called brabantite [4]. Monazite and brabantite can form continuous solid solutions [15] due to their similar crystal structures and very close cell parameters.

Absorption spectra of several plutonium (Pu) phosphates have been reported [16] and as expected [18] Pu^{3+} has been confirmed in the end member Pu monazite (PuPO$_4$) by optical spectroscopy. However, Pu^{4+} has been identified by optical spectrophotometry in Pu-doped LaPO$_4$ single crystals [17]. This result apparently contradicts the other studies in which Pu^{3+} was identified in directly substituted Pu monazite [4,18]. Early absorption spectroscopic studies generally were confined to wavenumbers >8000 cm^{-1}, thus failing to observe the f–f transitions in the mid near infrared. Recent X-ray diffraction work [19] on Pu monazites with Ca^{2+} as a charge compensator revealed that, depending on the oxygen partial pressure,

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both Pu^{3+} and Pu^{4+} ions can exist in brabantite at the same time, complementing earlier work by Vance et al. [12].

In the current work, we have used diffuse reflectance spectroscopy to study Pu valences in monazite, to try to resolve the above apparent contradiction, and to extend the absorption spectra data on Pu^{3+} and Pu^{4+} ions in monazite to the mid near infrared (4000 cm^{-1}).

2. Experimental

$La_{1-x}Pu_xPO_4$ and $La_{1-2x}Ca_xPu_xPO_4$ samples with x ranging from 0.01 to 0.1 were made by the standard oxide/nitrate route [20], calcined in air for 1 h at 750 °C and sintered for 16 h at 1500 °C in air. The samples were quite dilute in Pu to promote single-ion spectral behaviour.

As mentioned earlier, Pu^{4+} was found previously in Pu-doped $LaPO_4$ single crystals prepared by using the $Pb_2P_2O_7$ flux technique [17]. We considered the possibility that incorporation of small amounts of Pb^{2+} as the charge compensator could have led to the formation of Pu^{4+}. Thus, a monazite sample of $La_{0.96}Pb_{0.02}Pu_{0.02}PO_4$ stoichiometry was also prepared, by sintering in air at a relatively low temperature (1000 °C) to minimise Pb evaporation.

A Philips diffractometer was used for X-ray diffraction, employing Cu Kα radiation. All samples fired in air or reheated in argon showed only monazite-type X-ray reflections. Scanning electron microscopy (SEM) on polished surfaces of samples was carried out on a JEOL 6400 machine run at 15 kV and fitted with a Tracor Northern TN5502 energy-dispersive spectrometer (EDS) which utilised a comprehensive range of standards for quantitative work. SEM showed all samples were essentially single phase, although somewhat porous (see Fig. 1).
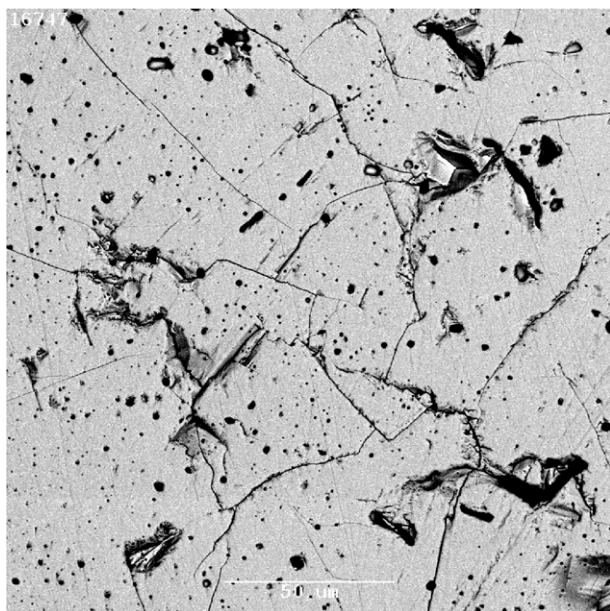
Pellet surfaces were coarsely polished with SiC paper to a 9.5 μm finish to assist diffuse reflectance. Diffuse reflectance (DR) spectra were collected on pellets at ambient temperature using a Cary 500 spectrophotometer equipped with a Labsphere Biconical Accessory. Spectra are referenced to that of a Labsphere certified standard (Spectralon), and transformed into Kubelka–Munk units, $F(R) = k/s = (1 - R)^2/2R$ [21–24], where R is reflectance; k and s are arbitrary constants, absorption and scattering coefficients (cm^{-1}), respectively. Therefore, the widely used remission (or Kubelka–Munk) function, $F(R)$, is proportional to the true absorption coefficient (k).

3. Results and discussion

3.1. Absorption spectra of Pu ions in $La_{1-x}Pu_xPO_4$

DR spectra, in the near infrared range, for Pu contents up to 0.1 formula units (f.u.) in monazites sintered in air are shown in Fig. 2. Most absorption bands increased in intensity with increasing Pu content, although Kubelka–Munk theory is not strictly followed insofar as the increase was not precisely linear with Pu content. DR spectra of Pu ions in the $La_{0.99}Pu_{0.01}PO_4$ sample sintered in air and reheated in argon are shown in Fig. 3. Both spectra look very similar except for a few additional bands marked by stars which appear on the spectrum of the sample sintered in air. Comparing them with published absorption spectra of Pu^{3+} and Pu^{4+} in both aqueous media [17,25,26] and in crystalline monazites [16,17], it is clear that the monazite sample sintered in air contains mainly Pu^{3+} but also some
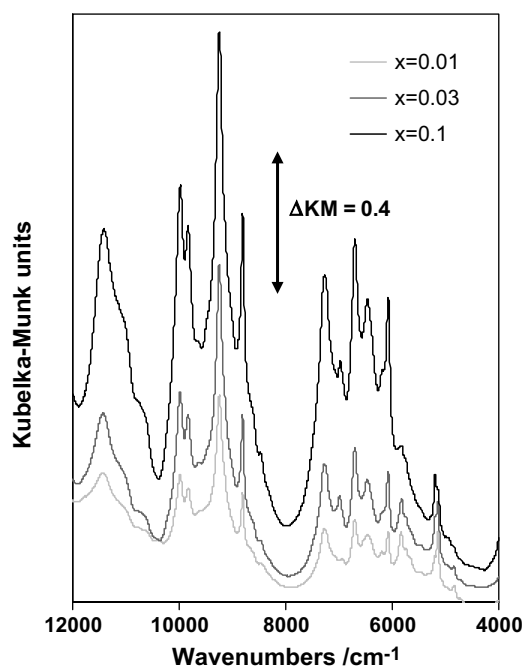

Fig. 1. SEM backscattered micrograph of the polished $Pu_{0.01}La_{0.99}PO_4$ sample shows it to be single phase, but with some porosity. Micrographs of the other samples were similar.

Fig. 2. DR spectra (4000–12000 cm^{-1}) of $La_{1-x}Pu_xPO_4$ ($x = 0.01$, 0.03 and 0.1) samples showing that most absorption bands increase in intensity with increasing Pu content.

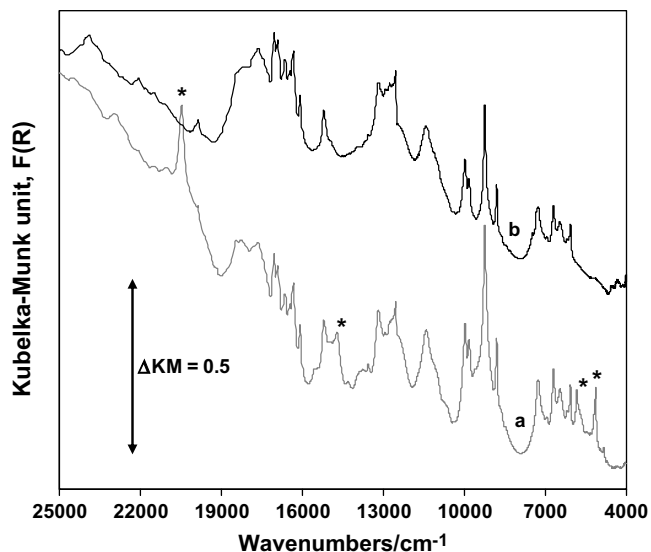Fig. 3. DR spectra (4000–25 000 cm^{-1}) of La$_{0.99}$Pu$_{0.01}$PO$_4$ sample: (a) sintered in air and (b) reheated in argon at 1400 °C for 2 h.

Pu^{4+} ions whereas the sample reheated in argon contains only Pu^{3+} ions. It will be shown below that the star-marked bands on the spectrum of the air-fired sample are attributable to Pu^{4+} ions. It is possible that small amounts of Pu^{4+} in the air-fired sample derive from the trace amounts of charge compensators or the formation of trace amounts of PuP$_2$O$_7$ [19].

3.2. Absorption spectra of Pu ions in La$_{0.96}$Ca$_{0.02}$Pu$_{0.02}$PO$_4$ and La$_{0.96}$Pb$_{0.02}$Pu$_{0.02}$PO$_4$

DR spectra of Pu ions in La$_{0.96}$Ca$_{0.02}$Pu$_{0.02}$PO$_4$ and La$_{0.96}$Pb$_{0.02}$Pu$_{0.02}$PO$_4$ samples sintered in air are shown in Fig. 4. The two spectra are very similar and represent typical absorption spectra of Pu^{4+} [16,25,26] and agree well with the data of Kelly et al. [17].
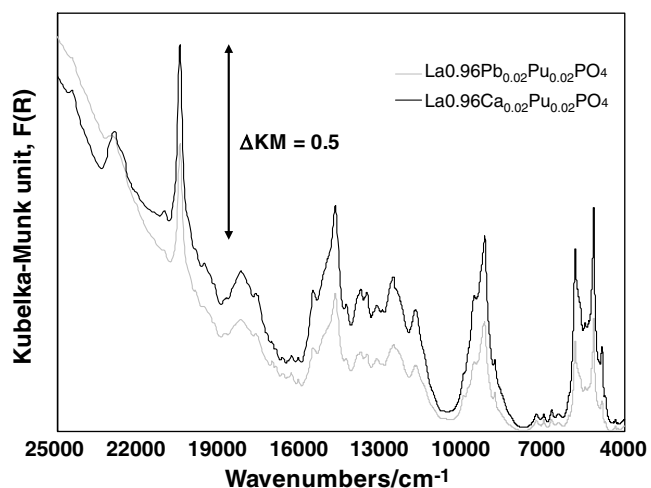

Fig. 4. DR spectra (4000–25 000 cm^{-1}) of La$_{0.96}$Ca$_{0.02}$Pu$_{0.02}$PO$_4$ sintered in air at 1500 °C and La$_{0.96}$Pb$_{0.02}$Pu$_{0.02}$PO$_4$ sintered in air at 1000 °C.
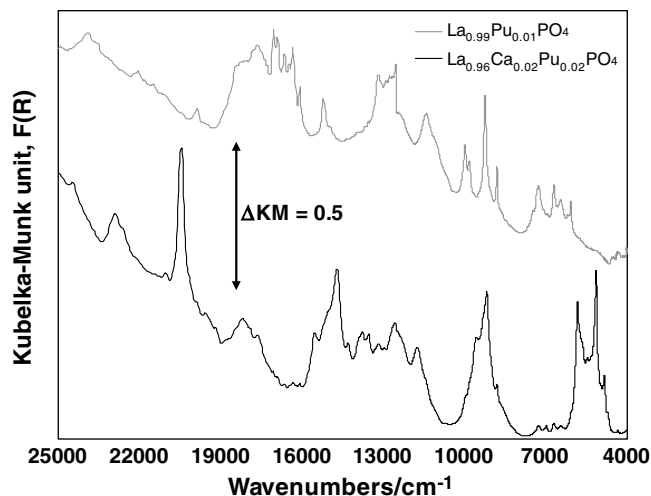
Fig. 5. DR spectra (4000–25 000 cm^{-1}) of La$_{0.99}$Pu$_{0.01}$PO$_4$ sintered in argon and La$_{0.96}$Ca$_{0.02}$Pu$_{0.02}$PO$_4$ sintered in air.

For comparison, DR spectra of Pu^{3+} ions in La$_{0.99}$Pu$_{0.01}$PO$_4$ sintered in argon and Pu^{4+} ions in La$_{0.96}$Ca$_{0.02}$Pu$_{0.02}$PO$_4$ sintered in air are shown together in Fig. 5. It is evident that the star-marked additional transition bands on the spectrum of air-fired La$_{0.99}$Pu$_{0.01}$PO$_4$ sample in Fig. 3 are attributable to the presence of Pu^{4+} ions. Moreover, the incorporation of Pb^{2+} (from the Pb$_2$P$_2$O$_7$ flux) in LaPO$_4$ single crystals is now understood to be the most likely reason that led to the formation of Pu^{4+} in the single crystals [17]. Heating these samples for 2 h in argon at 1200 °C had no significant effect on the DR spectra.

4. Conclusions

We have demonstrated using optical spectroscopy that without presence of charge compensators Pu exists mainly as Pu^{3+} ions in monazites fired in air and only Pu^{3+} ions in those fired in argon. We have shown that the incorporation of small amounts of Pb^{2+} is the likely case of the formation of Pu^{4+} in Pu-doped LaPO$_4$ single crystals reported previously [17], and a similar result was obtained using Ca^{2+} as a charge compensator for Pu^{4+}. The absorption spectra of both Pu^{3+} and Pu^{4+} ions in monazite have been extended to the mid near infrared region to allow the Stark components of the lowest manifold to be determined. The majority of the f–f electronic transitions in the near infrared increase with increasing of Pu contents to ∼0.1 f.u., although Kubelka–Munk behaviour is not strictly followed.

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