

Crystal chemistry of REEXO₄ compounds (X = P, As, V). II. Review of REEXO₄ compounds and their stability fields

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Abstract: A comprehensive critical review of the phase fields, metastable modifications, solid solution ranges and phase transitions of monazite- and zircon-type REEXO₄ (X = P, As, V) compounds is given. Monazite-type REEPO₄ compounds are stable for REE = La to Gd and metastable for Tb to Ho; zircon-type members exist for REE = Gd to Lu, and Y, Sc. REEAsO₄ compounds with monazite-type structure exist for REE = La to Nd, while zircon-type compounds are known for REE = Pm to Lu, and Y, Sc; no metastable arsenate members are known. The only stable monazite-type REEVO₄ is LaVO₄, but metastable members are known for REE = Ce to Nd. Zircon-type REEVO₄ compounds are stable for REE = Ce to Lu, and Y, Sc, and metastable for REE = La. Solid solution series are complete only if minor size differences exist between REE³⁺ or X⁵⁺ cations in respective end-members. Phase transitions occur under pressure (zircon → (monazite →) scheelite) and at very low temperatures. The evaluation of the metastable phase fields and of naturally occurring members suggests that metastable modifications of REEXO₄ compounds can occur in nature under certain conditions (formation at temperatures < ~200-300°C; formation via hydrated precursor phases; stabilisation by various impurity cations).

Key-words: REEXO₄ compounds, review, monazite, xenotime, zircon, stability, phase transition.

Introduction

The present article is the second part of studies of the crystal chemistry of REEXO₄ compounds (X = P, As, V). In the first part (the accompanying paper by Kolitsch *et al.*, 2004), we present data on the paragenesis and crystal structure of a phosphatian gasparite-(Ce) [ideally CeAsO₄] from Kesebol, Sweden. Apart from the important role of phosphate members in the geosciences, all REEXO₄ compounds are also of increasing importance in several related fields of science. The physico-chemical properties of monazite-type synthetic REEPO₄ compounds have been studied in some depth in the last two decades. These phosphates are non-toxic, and LaPO₄-Al₂O₃ composite ceramics with excellent high-temperature properties, and high damage tolerance, machinability and oxidation resistance have been characterised (*e.g.*, Davis *et al.*, 1998, 2000; Marshall *et al.*, 1999, and references therein). Similarly good high-temperature properties are known for the zircon-type REEPO₄ (Hikichi *et al.*, 1998). Freezing points for some REEPO₄ phases range between 1896°C (REE = Er) and 2072°C (REE = La) (Hikichi *et al.*, 1979, 1987; Hikichi & Nomura, 1987). Melting points of members along the series REEAsO₄ (REE = La-Lu) are also very high and increase from 1830°C to 2000°C (Angapova & Serebrennikov, 1973).

REEPO₄ materials have been proposed as important candidates for host materials suitable for the stabilisation and disposal of high-level nuclear waste (*e.g.*, Boatner *et al.*, 1980; McCarthy *et al.*, 1980; Pepin *et al.*, 1981; Volkov, 1999; Meldrum *et al.*, 2000; Ewing, 2001; Ewing & Wang, 2002). Furthermore, REEPO₄ compounds show intense blue photoluminescence (*e.g.*, Aia, 1967), and they are promising scintillators, especially if doped with Ce, Eu or Sm (*e.g.*, Lempicki *et al.*, 1993; Wojtowicz *et al.*, 1995; Moses *et al.*, 1998). GdPO₄ is an excellent candidate for a chemically stable, water-insoluble neutron absorber for inclusion in spent nuclear fuel canisters (Lessing & Erickson, 2003). Interestingly, both REEPO₄ phases and their arsenate and vanadate analogues were found to be ferroelectrics for most REE members (*e.g.*, Ismailzade *et al.*, 1980, 1981; Kurbanov *et al.*, 1982; Hur *et al.*, 1990). Nd-doped YVO₄ is one of the most interesting laser hosts for micro and diode-pumped solid state lasers (*e.g.*, Guillot-Noel *et al.*, 2000). Recently, REEVO₄ materials were reported to be efficient for the catalytic treatment of propane (*e.g.*, Au & Zhang, 1997) and hydrogen sulphide (Li & Chi, 2001).

The present article provides a comprehensive review of the monazite- and zircon-type phase fields (stable and metastable), as well as solid solution ranges and phase transitions of REEXO₄ (X = P, As, V) compounds. Furthermore, impor-

tant implications for the observation of metastable REEXO₄ modifications in nature are pointed out.

Review of REEXO₄ compounds and their stability fields

Although a large amount of literature exists on REEXO₄ compounds (both natural and synthetic), no up-to-date and complete review is available. Furthermore, the published reports are scattered in very different journals, and authors were often unaware of previous work, partially resulting in duplicate results. The present review restricts itself to REEXO₄ compounds where REE = rare-earth elements (including Y and Sc) and X = P, As, V. Here are excluded the monazite-type compounds with the general formula AXO₄ where A = divalent metal and X = S, Cr, or where A = tetravalent metal and X = Si, Ge (e.g., huttonite, ThSiO₄), and monazite-type YbBeF₄ (Köhler, 1999). Our discussion focusses on the monazite-type (sometimes also referred to as huttonite-type) and zircon-type structures (sometimes also referred to as xenotime-type), and does not include fergusonite- and scheelite-type A³⁺B⁵⁺O₄ compounds (e.g., Loskutov *et al.*, 1977; Aldred, 1984a). Moreover, those references containing spectroscopic data or reporting magnetic and thermodynamic properties are not included, except when useful for the discussion. The present review first provides a concise summary of the stability fields among the three series of REEXO₄ compounds, including a discussion of metastable phases. This review is followed by a compilation and critical discussion of the observed solid solutions, and phase transitions at high pressures and very low temperatures. Finally, important implications for occurrences of REEXO₄ compounds in natural environments are discussed.

REEPO₄, REEAsO₄ and REEVO₄ compounds

The crystal chemistry of REEPO₄ compounds was investigated by a multitude of authors (Mooney, 1948, 1956; Carron *et al.*, 1958; Schwarz, 1963a; Feigelson, 1964; Weigel *et al.*, 1965a and b; Ivanov & Sin'kova, 1967; Patscheke *et al.*, 1968; Hintzmann & Müller-Vogt, 1969; Kuznetsov *et al.*, 1969; Repko *et al.*, 1971; Jaulmes, 1972; Wanklyn, 1972; Lohmüller *et al.*, 1973; Ropp & Carroll, 1973; Hikichi & Hukuo, 1975; Bondar *et al.*, 1976; Kizilyalli & Welch, 1976; Baran, 1978; Hikichi *et al.*, 1978; Orlovskii *et al.*, 1978; Yurchenko *et al.*, 1978; Beall *et al.*, 1981; Pepin & Vance, 1981; Milligan *et al.*, 1982, 1983a, b and c; Aldred, 1984a, b and c; Mullica *et al.*, 1984, 1985a and b; Nekrasova *et al.*, 1985; Jonasson & Vance, 1986; Kurbanov *et al.*, 1986; Mullica *et al.*, 1986b; Hikichi, 1988; Hikichi *et al.*, 1988; Jonasson *et al.*, 1988; Nekrasova *et al.*, 1988; Rudenko *et al.*, 1988; Montel *et al.*, 1989; Hikichi, 1991; Hikichi *et al.*, 1990, 1991, 1993; Inoue *et al.*, 1993; Rasmussen *et al.*, 1993; Ni *et al.*, 1995; Rosenblum & Fleischer, 1995; Hikichi, 1996; Hikichi *et al.*, 1997; Bernhard *et al.*, 1998; Hikichi, 2001; Ushakov *et al.*, 2001; Boatner, 2002; Celebi & Kolis, 2002; Moëlo *et al.*, 2002; Donovan *et al.*, 2003; Lessing & Erickson, 2003). There is general agreement that the

members containing larger REE have the monazite structure, whereas those members with smaller REE (including Y and Sc) crystallise with the zircon-type structure. Although the boundary between the structure types is usually assumed to lie between Gd and Tb, an assumption based on a very early review (Carron *et al.*, 1958, and references cited therein), this is not generally true because the structure type observed depends strongly on the conditions of formation (mainly preparation temperature and properties of the precursor material). This was first realised by Ivanov & Sin'kova (1967) who synthesised Gd-, Tb-, Dy- and Ho-phosphates with both monazite- and zircon-type structures, and concluded that the main factors controlling the preference of the structure type were the temperature of preparation and the pH of the solution from which the phosphates precipitated. This dimorphism was confirmed by later work on TbPO₄ (Baran, 1978; Nekrasova *et al.*, 1988) and REEPO₄ where REE = Gd, Tb and/or Dy (Bondar *et al.*, 1976; Kizilyalli & Welch, 1976; Jonasson & Vance, 1986; Hikichi, 1988; Hikichi *et al.*, 1988, 1993; Inoue *et al.*, 1993; Ushakov *et al.*, 2001). Earlier work by Schwarz (1963a) demonstrates that monazite-type TbPO₄ above 1000°C slowly transforms into the zircon-type structure. Zircon-type GdPO₄ can form upon dehydration of synthetic, churchite-type GdPO₄·2H₂O (As-saaoudi *et al.*, 2000) and has also been prepared hydrothermally at 400°C (Celebi & Kolis, 2002). Flux growth of GdPO₄ resulted in both monazite- and zircon-type crystals (Ushakov *et al.*, 2001), and annealing of monazite-type samples in air at 1600°C for 7 h did not result in a complete transformation to the zircon-type modification. However, according to Bondar *et al.* (1967) monazite-type GdPO₄ transforms into its zircon-type dimorph at ~1700°C. Heating of synthetic GdPO₄·1H₂O in flowing air to temperatures between 800 and 1400°C yielded only monazite-type GdPO₄, although differential thermal analysis showed small peaks in the 1200–1250°C range, that could possibly indicate a reversible, very rapid monazite ↔ zircon phase change (Lessing & Erickson, 2003). Thus, the data on GdPO₄ are inconclusive.

Nonetheless, a general observation of the authors of the cited articles was that the “metastable” monazite-type modifications always transformed to the stable zircon-type modifications after heating between approximately 300 and 1100°C. No thermodynamically corroborated transition temperatures are known yet. However, recent accurate measurements of the enthalpies of formation for all REEPO₄ compounds (Ushakov *et al.*, 2001) show that the enthalpy values become more negative with increasing REE³⁺ ionic radius; from these results, the authors concluded that the monazite structure is thermodynamically metastable for TbPO₄ and DyPO₄, and that the change of structure from zircon-type to monazite-type does not significantly affect the energetic trend. The latter observation is explained by the close relation between the monazite and zircon structures (for details see Ni *et al.*, 1995; Boatner, 2002).

There exists a much smaller number of previous studies on REEAsO₄ compounds. These studies all agree that only the members with La, Ce, Pr and Nd have the monazite structure, whereas the remaining members (REE = Pm-Lu, Y, Sc) crystallise in the zircon-type structure (Durif & Forrat, 1957; Carron *et al.*, 1958; Schwarz, 1963a and b; Weigel

& Scherer, 1967; Feigelson, 1967; Hintzmann & Müller-Vogt, 1969; Lohmüller *et al.*, 1973; Ropp & Carroll, 1973; Angapova & Serebrennikov, 1973; Escobar & Baran, 1978a; Smith *et al.*, 1978; Gabisoniya & Nanobashvili, 1980; Botto & Baran, 1982; Wanklyn *et al.*, 1984; Mullica *et al.*, 1986b; Choudhary, 1991; Choudhary & Yadav, 1992, Brahim *et al.*, 2002). Specifically, for NdAsO₄ no evidence for a (high-temperature) zircon-type modification was found even when REEAsO₄ members were precipitated at low-temperatures, or prepared by dehydration of REE arsenate hydrates (Durif & Forrat, 1957; Schwarz, 1963b; Angapova & Serebrennikov, 1973; Escobar & Baran, 1978a). Because these low-temperature techniques of preparation usually lead to metastable modifications (compare the above data on REEPO₄ and below on REEVO₄), Escobar & Baran (1978a) pointed out that the behaviour of the REE-AsO₄ compounds is surprisingly different from those of the REEPO₄ compounds. Consequently, it has been predicted that only PmAsO₄ exhibits dimorphism (Escobar & Baran, 1978a; Ropp & Carroll, 1973), although so far only a zircon-type modification of PmAsO₄ has been reported (Weigel & Scherer, 1967).

REEVO₄ compounds have been studied by a large number of authors (Milligan *et al.*, 1949; Milligan & Vernon, 1952; Milligan *et al.*, 1953; Durif, 1956; Carron *et al.*, 1958; Naumov, 1962; Gambino & Guare, 1963; Schwarz, 1963a; Brixner & Abramson, 1965; Baglio & Gashurov, 1968; Feigelson, 1968; Patscheke *et al.*, 1968; Hintzmann & Müller-Vogt, 1969; Yoshimura & Sata, 1969; Sato & Utsunomiya, 1970; Baglio & Sovers, 1971; Baran & Aymonino, 1971; Brusset *et al.*, 1971; Fuess & Kallel, 1972; Glazyrin & Borisenko, 1972; Lohmüller *et al.*, 1973; Ropp & Carroll, 1973; Bazuev *et al.*, 1974; Smith *et al.*, 1974; Rice & Robinson, 1976; Bazuev *et al.*, 1978; Escobar & Baran, 1978b; Rykova *et al.*, 1979; Udalov & Appen, 1982; Aldred, 1984b, c; Dabkowski *et al.*, 1985; Baudracco-Gritti *et al.*, 1987; Chakoumakos *et al.*, 1994; Howard *et al.*, 1995; Osawa *et al.*, 1996; Mullica *et al.*, 1996b; Damon *et al.*, 2002; Schmidt *et al.*, 2002; Varma *et al.*, 2002). There is general agreement that LaVO₄ prepared by high-temperature solid-state synthesis or flux growth, is the only REEVO₄ compound crystallising in the monazite-type structure, whereas all other REE members (Ce-Lu, Y, Sc) exhibit the zircon-type structure. However, monazite-type REEVO₄ (REE = Ce, Pr, Nd) could be obtained by the atmospheric oxidation of the corresponding REEVO₃ compounds at 350-400°C (Bazuev *et al.*, 1974). Similarly, metastable monazite-type CeVO₄ was observed by Yoshimura & Sata (1969) as an oxidation product of CeVO₃. It was also reported that the structure of LaVO₄ depends on the mode of preparation (Ropp & Carroll, 1973; Bazuev *et al.*, 1974; Escobar & Baran, 1978b); for example, Ropp & Carroll (1973) observed that LaVO₄ precipitated from solution has the zircon-type structure, but after heating above ca. 300°C converts into the monazite-type form. Damon *et al.* (2002) even observed that the pH of solutions from which LaVO₄ is precipitated, has an influence on the structure of the precipitate: single-phase monazite-type LaVO₄ only crystallised at pH = 9, whereas at pH = 5-8 a mixture of both monazite-type and zircon-type LaVO₄ was obtained. Hydrothermally synthesised LaVO₄ has the zircon-

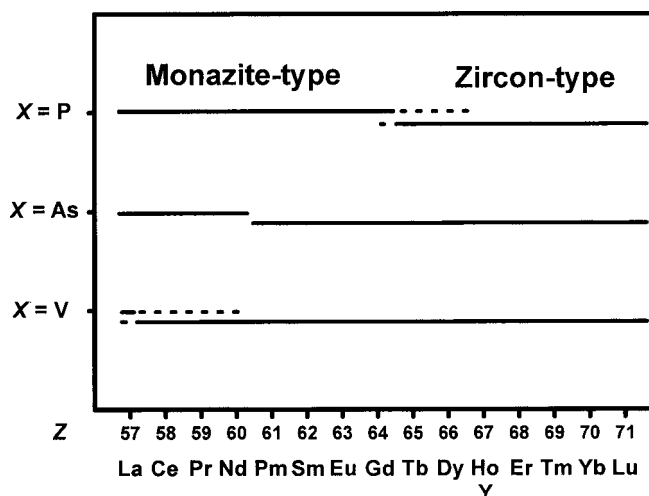


Fig. 1. Stability fields of the monazite and zircon structure types among REEXO₄ (X = P, As, V) compounds (dotted lines = metastable regions). Note that Y (Z = 39) is grouped with Ho because Y³⁺ and Ho³⁺ ions have nearly identical radii. Sc (Z = 21) is not shown because it yields only zircon-type compounds. Data on the stable high-temperature modification of GdPO₄ are inconclusive (see text). PmAsO₄ is assumed to be dimorphous but at present only the zircon-type modification is known (see text).

type (Oka *et al.*, 2000). Ongoing work on a new mineral with a near-end-member LaVO₄ composition (La-analogue of wakefieldite-(Ce)); work by Witzke, Kolitsch and co-workers) showed that it has the zircon structure type. Very recently, Varma *et al.* (2002) synthesised mixed orthovanadates La_{1-x}Ce_xVO₄ by solid-state reaction at 600°C, and demonstrated that a monazite-type LaVO₄ phase was retained for the samples with x ≤ 0.2, while the zircon-type CeVO₄ was stabilised for x ≥ 0.5. In the intermediate range 0.2 < x < 0.5, both LaVO₄ and (zircon-type) La_{0.5}Ce_{0.5}VO₄ co-existed.

On the basis of available data on REEXO₄ (X = P, As, V) compounds, it is possible to construct a schematic diagram showing (meta-)stability fields of the monazite and zircon structure types (Fig. 1), that allows the following important conclusions: (i) within a single series of REE phosphates, arsenates or vanadates, the monazite structure type is stable for the large(r) REE³⁺ cations, whereas the small(er) REE³⁺ cations form the zircon structure; (ii) the stability field of the monazite structure type in REEXO₄ (X = P, As, V) compounds narrows with increasing size of the XO₄ group (Fig. 1). This structural influence of the XO₄ group is in agreement with earlier conclusions of Losutov *et al.* (1977) that an increase of the ionic radius of the X atom in AXO₄ compounds ultimately leads to the structure types of scheelite and, for very large X atoms, of wolframite; (iii) metastable phase fields are evident for the areas left and right of the monazite-zircon structure-type 'boundary' (Fig. 1). These metastable regions are largest for the phosphates and absent for the arsenates. Ropp & Carroll (1973) found, in an early comparison of the (then known) dimorphic forms of REE-XO₄ compounds (*i.e.*, TbPO₄ and LaVO₄), a linear correlation between the REE³⁺ radius and the X⁵⁺ radius of the

$(XO_4)^{3-}$ tetrahedral oxyanion rather than with the $X-O$ bond length or the tetrahedral volume of the oxyanion. The observation of Ropp & Carroll (1973) was based on the assumption that $PmAsO_4$ is also dimorphic. However, the existence of monazite-type $PmAsO_4$ has not been demonstrated yet.

No reliable thermodynamic data for the $REEAsO_4$ or $REEVO_4$ series have been reported yet, although calculated values for standard thermodynamic functions for the arsenate members are given by Kasenov & Sharipova (1991a and b, 1994).

The known mineral species representative of the REE phosphate, arsenate and vanadate series are the five monazite-type minerals monazite-(La), -(Ce), -(Nd), -(Sm) (Masau *et al.*, 2001, 2002) and gasparite-(Ce), and the six zircon-type species xenotime-(Y), -(Yb), pretulite [$ScPO_4$], chernovite-(Y) [$YAsO_4$], and the very rare vanadate members wakefieldite-(Y) and -(Ce).

Solid solutions in the systems $REEXO_4$ ($X = P, As, V$)

Synthetic solid solutions in the systems $REEXO_4$ ($X = P, As, V$) have been studied by a relatively small number of authors, based on samples prepared by different methods. These studies predominantly involved material in which either one specific REE or X atom was replaced by another. Feigelson (1967) prepared $(REE,REE')AsO_4$ and $REE(As,P)O_4$ compositions by the flux method. He observed that a zircon-type modification of $NdAsO_4$ (not stable if chemically pure, see previous section) can be stabilised if Sm is allowed to substitute for Nd, as testified by the growth of zircon-type $Nd_{0.65}Sm_{0.35}AsO_4$ crystals. Flux-grown zircon-type $Dy(As_xV_{1-x})O_4$ crystals were characterised by Taylor *et al.* (1990) who noted highly homogeneous chemical compositions. Tananaev *et al.* (1971) synthesised various mixed (LREE,HREE) phosphate members also by the flux method, and observed a limited substitution of Nd into YPO_4 , synthetic xenotime-(Y). A study of the system YVO_4 - YPO_4 revealed a complete solid-solution range and strict adherence to Vegard's law (Ropp & Carroll, 1975). In a series of papers, Mullica and co-workers synthesised various mixed $(REE,REE')PO_4$ members with fixed stoichiometries ($REE:REE' = 1:1$ or $3:1$) (Mullica *et al.*, 1986a, 1990, 1992, 1996a).

In all these cases, the symmetry of the solid-solution members was that expected from the known solid solution ranges for the monazite and zircon types and the average radius of the atoms on the REE site. When several REE were allowed to simultaneously substitute for Ce in $CePO_4$, ideal solid-solution behaviour and adherence to Vegard's law were observed (Nekrasov & Novikov, 1991). Similar observations were also made for the complete isostructural solid solution series $Nd_xYb_{1-x}VO_4$ ($x = 0-1$) (Glazyrin & Borisenko, 1972), the system $REE(V_xP_{1-x})O_4$ (Aldred, 1984c), the zircon-type $Dy(As_xV_{1-x})O_4$ crystals (Taylor *et al.*, 1990), as well as the series $Ce_xGd_{1-x}PO_4$ (Gratz & Heinrich, 1998).

When the end-members are not isostructural, restricted solubility ranges are observed. For the system $REE(V_xP_{1-x})O_4$ these ranges and their systematic change were characterised by Aldred (1984c). A recent study of the

system $(Ce,Y)PO_4$ (Gratz & Heinrich, 1997) reported a temperature-dependent miscibility gap; as expected, the solubility of YPO_4 in $CePO_4$ was considerably higher than *vice-versa*. The REE partitioning in hydrothermally synthesised $(Y,REE)PO_4$ solid-solution phases (monazite-xenotime pairs) was investigated by Andrehs & Heinrich (1998) who noted a pronounced influence of REE^{3+} ionic radius and temperature. The occurrence of both monazite- and zircon-type phases in mixed orthovanadates $La_{1-x}Ce_xVO_4$ (Varma *et al.*, 2002) has already been noted above. The three papers just mentioned represent rare examples of more comprehensive studies of the accurate solid solubility limits in $REE-XO_4$ solid solutions. The available data demonstrate that, in general, the larger the difference in radii of the two REE^{3+} ions in a given $(REE,REE')XO_4$ system, the lower the extent of mutual REE substitution. A higher level of both HREE substitution in monazite phases and LREE substitution in xenotime phases was found in synthetic samples heated to $1500^\circ C$ (Van Emden *et al.*, 1998). Interestingly, synthetic xenotime phases containing Y in combination with smaller LREE, which were heated at $1500^\circ C$, show some evidence of REE cationic ordering, but this behaviour has not yet been well characterised (Van Emden *et al.*, 1998). No anionic ordering has been described so far for synthetic $REE-(PO_4,VO_4)$ solid-solution members (see, *e.g.*, the detailed study of Aldred, 1984c).

Natural occurrences representative of the solid solution series between xenotime-(Y) [YPO_4] and chernovite-(Y) [$YAsO_4$] are known from the famous Binn Valley, Valais, Switzerland (*e.g.*, Graeser *et al.*, 1973; Graeser, 1995; Graeser & Albertini, 1995). In our accompanying paper (Kolitsch *et al.*, 2004) we have shown that a gasparite-(Ce) [ideally $CeAsO_4$] from Kesebol, Sweden has more than 10 % of its As substituted by P. Apparently, no comprehensive or systematic studies of the quantitative influence of a PO_4 - AsO_4 substitution on the resulting structure type for $REE-(As,P)O_4$ solid solutions have been conducted yet.

Reported phase transitions

At elevated pressures REE phosphates show no change in structure type, whereas the majority of the investigated REE arsenates and vanadates undergo a reconstructive transformation from the zircon-type structure (space group $I/4_1amd$) to a scheelite-type structure (space group $I/4_1a$) ($REEAsO_4$ where $REE = Sm-Lu$, and $REEVO_4$ where $REE = Pr-Lu, Y$; Stubican & Roy, 1963a and b; Jayaraman *et al.*, 1987; Range & Meister, 1990). A monazite \rightarrow scheelite transformation has been observed for $PrAsO_4$ and $NdAsO_4$ (Stubican & Roy, 1963a), whereas a zircon \rightarrow monazite \rightarrow scheelite transformation has been reported for $CeVO_4$ (Range *et al.*, 1990). Interestingly, scheelite-type $NdAsO_4$ has also been prepared from component oxides at $550^\circ C$ in an evacuated silica ampoule (Mazhenov *et al.*, 1988).

Several zircon-type $REEAsO_4$ and $-VO_4$ compounds show phase transitions below 20 K and interesting magnetic properties; low-temperature studies on $SmAsO_4$, $DyAsO_4$, $TbAsO_4$, $TbVO_4$ and $DyVO_4$ and their cooperative Jahn-Teller phase transitions were reported by a number of au-

thors such as, for instance, Forsyth & Sampson (1971), Klein *et al.* (1971), Schäfer & Will (1971), Will *et al.* (1971), Göbel & Will (1972a and b), Will *et al.* (1972), Berkahn *et al.* (1973), Harley *et al.* (1974), Wappler (1974), Long & Stager (1977), Domann & Kasten (1979), Schäfer & Will (1979), Page *et al.* (1979), Domann *et al.* (1980), Kasten (1980), Nägele *et al.* (1980) and Page *et al.* (1984) (see also Bowden, 1998, Chakrabarti *et al.*, 1999, Kirschbaum *et al.*, 1999, Bleaney, 2000, and references therein). These studies show that the low-temperature modification of DyAsO₄ crystallises in space group *Imma*, and that of TbAsO₄ in *Fddd*. A Jahn-Teller induced phase transition of TbVO₄ at 33 K to *Fddd* has recently been reported by Kirschbaum *et al.* (1999).

Implications for the natural occurrence of REEXO₄ compounds

From the critical summary of the stable and metastable phase fields discussed above, important implications for the natural occurrence of REEXO₄ compounds in different geologic environments can be inferred. Firstly, if natural REEXO₄ compounds crystallise at low temperatures (< ca. 200–300°C) and/or *via* hydrated precursor phases (*e.g.*, rhabdophane-type REEXO₄·1H₂O or churchite-type REEXO₄·2H₂O), metastable zircon-type or, less probably, monazite-type modifications can originate. These metastable phases can persist for long times, unless subjected to later higher temperatures (*e.g.*, during metamorphic processes).

There are already various known examples for low-temperature genesis of natural monazite. For instance, both monazite-(Ce) and -(La) occur as small sprays of acicular crystals formed under low-temperature hydrothermal conditions in a barite-fluorite vein, Black Forest, Germany (Walenta, 1987, 1992; Kolitsch, unpublished data, and Kolitsch & Göttinger, 2000, respectively). Pseudomorphs of monazite-(Ce) formed under supergene conditions were also reported from the same locality (Walenta, 1987). Rare diagenetic and authigenic formations of monazite-(Ce) and/or xenotime in sediments such as silts, shales, turbidites, sandstones, metacherts and karst-bauxites have been described (*e.g.*, Donnot, 1973; Lefebvre & Patterson, 1982; Cooper *et al.*, 1983; Nekrasova & Nekrasov, 1983; Evans & Zalasiewicz, 1996; Maksimović & Pantó, 1996; Lev *et al.*, 1998; Rasmussen *et al.*, 1998; Cabella *et al.*, 2001; England *et al.*, 2001; Sankaran, 2001). Moreover, occurrences of some unnamed and insufficiently characterised REE arsenate members, which have partly formed under low-temperature conditions, are mentioned in the Introduction part of our accompanying paper (Kolitsch *et al.*, 2004).

A second implication is that the substitution of REE³⁺ ions for differently sized REE³⁺ ions in natural REEXO₄ compounds can lead to the stabilisation of otherwise unstable (end-member) modifications, depending on the average REE³⁺ ionic radius in the respective samples. It is noteworthy that both anhydrous and hydrated REEPO₄ minerals undergo selective surface ion-exchange (REE ↔ REE') reactions with aqueous solutions at low temperatures (Jonasson *et al.*, 1998). A further influence on stabilities could be the

possible presence of commonly observed impurity elements such as Ca, U, Th, Si, etc. in natural samples (see, for instance, Demartin *et al.*, 1991a and b, the compilations by Rosenblum & Fleischer, 1995, and Boatner, 2002, and references therein). The natural occurrence of an Y-dominant, monazite-type (Y,REE)PO₄ mineral might be possible, because metastable monazite-type compounds such as synthetic DyPO₄ and HoPO₄ have been reported (see above and Fig. 1), and because Y³⁺ and Ho³⁺ (and Dy³⁺) ions have nearly identical ionic radii.

The obvious third implication is that the substitution of one or more X⁵⁺ cation for a differently sized X⁵⁺ cation could result in similar stabilisation effects. Again, the influence of additional impurity elements on the X site (*e.g.*, Si and S) has to be taken into account.

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