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Crystal chemistry of REEXO_4 compounds (X = P, As, V). II. Review of REEXO_4 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 REEXO_4 (X = P, As, V) compounds is given. Monazite-type $REEPO_4$ 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. $REEAsO_4$ 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 $REEVO_4$ is $LaVO_4$, but metastable members are known for REE = Ce to Nd. Zircon-type $REEVO_4$ 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 REE^{3+} or X^{5+} 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 REEXO_4 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: REEXO_4 compounds, review, monazite, xenotime, zircon, stability, phase transition.

Introduction

The present article is the second part of studies of the crystal chemistry of REEXO_4 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 $CeAsO_4$] from Kesebol, Sweden. Apart from the important role of phosphate members in the geosciences, all REEXO_4 compounds are also of increasing importance in several related fields of science. The physico-chemical properties of monazite-type synthetic $REEPO_4$ compounds have been studied in some depth in the last two decades. These phosphates are non-toxic, and $LaPO_4$-Al_2O_3 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 $REEPO_4$ (Hikichi *et al.*, 1998). Freezing points for some $REEPO_4$ 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 $REEAsO_4$ (REE = La-Lu) are also very high and increase from 1830°C to 2000°C (Angapova & Serebrennikov, 1973). $REEPO_4$ 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, $REEPO_4$ 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). $GdPO_4$ is an excellent candidate for a chemically stable, water-insoluble neutron absorber for inclusion in spent nuclear fuel canisters (Lessing & Erickson, 2003). Interestingly, both $REEPO_4$ 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 YVO_4 is one of the most interesting laser hosts for micro and diode-pumped solid state lasers (*e.g.*, Guillot-Noel *et al.*, 2000). Recently, $REEVO_4$ 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 REEXO_4 (X = P, As, V) compounds. Furthermore, impor-

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