

the crystal structures of both, quasicrystals and their approximants.

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#### FLUX GROWTH, COMPOSITION AND MORPHOLOGY OF RARE EARTH DOPED $\text{KLu}(\text{WO}_4)_2$ CRYSTALS

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Potassium rare earth tungstate single crystals are highly efficient materials for diode-pumped solid-state lasers, Raman shifters, planar waveguide devices and other industrial applications. In this paper, a correlation between growth conditions, composition, physical properties and morphology of crystals grown is discussed for several representatives of this family.

Potassium lutetium tungstate crystals have been successfully grown by top seeded solution growth method. Using BFDH law and PBC theory, an ideal habit of these crystals has been calculated. The crystal structure of  $\text{KLu}(\text{WO}_4)_2$  was refined. Absorption and fluorescence spectra of  $\text{Tb:KLu}(\text{WO}_4)_2$  were measured at room temperature. The specific heat is a little lower in comparison with  $\text{Yb:KLu}(\text{WO}_4)_2$  at 90°C. Spectral and luminescent properties of the  $\text{Sm:KLu}(\text{WO}_4)_2$  crystal have been investigated. Based on the Judd–Ofelt theory, the spectral parameters have been obtained as the followings: the phenomenological intensity parameters  $\Omega_\lambda$ , are:  $\Omega_2 = 15.72 \times 10^{-20} \text{ cm}^2$ ,  $\Omega_4 = 4.223 \times 10^{-20} \text{ cm}^2$  and  $\Omega_6 = 2.839 \times 10^{-20} \text{ cm}^2$ , irradiative transition probabilities  $A_{ij}$ , and oscillator strengths  $P_{ij}$ . The irradiative lifetime of levels  ${}^4G_{5/2}$  is 748 ms. In addition, the values of integrated emission cross sections are also calculated.

Growth mechanisms of  $\text{KLu}(\text{WO}_4)_2$  crystals have been investigated using ex situ atomic force microscopy. 2D nuclei and spiral hillocks are simultaneously imaged on the {110} faces. It was presumed that both screw dislocation sources and 2D nucleus on the {110} faces as well as simple flow of steps on {310} faces are responsible for the faceting and habit of  $\text{KLu}(\text{WO}_4)_2$  crystals grown from  $\text{K}_2\text{W}_2\text{O}_7$  based high-temperature solutions. A special dislocation sources with the Burgers vectors perpendicular to the {110} crystal face of b =

8 are also discussed.

The composition of crystals grown was measured by the microprobe analyzer CAMECA SX-50 with an accuracy of  $\pm 0.02\text{-}0.03\text{wt}\%$ . The segregation coefficients (K) were calculated basing the following equation  $K = C_{\text{cryst}}/C_{\text{dissKReW}}$  where  $C_{\text{cryst}}$  is Re content in grown crystals and  $C_{\text{dissKReW}}$  is Re concentrations in the corresponding crystalline substances of the fluxed melt. It was found that the average K value vary from 0.80 to 1.02.

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#### PRACTICAL CRYSTAL GROWTH IN SILICA HYDROGELS: APPLICATION TO THE SYNTHESIS OF INSOLUBLE URANYL PHASES

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Crystal growth in gels is a particular case of crystallization from solution [1, 2]. However, because of the physical nature of gel media, crystal growth is controlled by the process of diffusion, whereas convection and sedimentation are completely suppressed. For these reasons, crystallization in gels is an excellent method to grow high-quality crystals of materials that have both low solubility and low thermal stability [3, 4]. This submission reviews the practical growth of crystals in gel media with the examples of uranyl phosphate (and arsenate) hydrates.

A gel may be defined as a semi-rigid solid resulting from the colloidal suspension of a solid dispersed in a liquid. The gel considered in this work is a silica hydrogel: a two-component medium in which a microporous flexible network of polymerized silica is continuously permeated by an aqueous phase [1, 2]. Historically, silica hydrogel was commonly produced from the careful neutralization of aqueous sodium metasilicate with strong acid. Aside from the difficulty of preparation, a major disadvantage of this method is the high sodium content of the resulting gel [3-5]. A simpler and faster method that produces alkali-free gel is through the polycondensation in water of silicon alkoxides such as tetramethoxysilane,  $(\text{CH}_3\text{O})_4\text{Si}$ , or tetraethoxysilane,  $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$  [5, 6].

Tetramethoxysilane (TMS) is almost completely immiscible with water. A silica hydrogel with a density close to water (1.003 g/mL) is easily produced by rapidly stirring a mixture of 10 volume% TMS (density 1.023 g/mL) with 90% aqueous solution for a short period (usually 5-15 minutes) until only one phase is observable. The idealized chemical reaction leading to the formation of the gel is:  $(\text{CH}_3\text{O})_4\text{Si} + 2 \text{H}_2\text{O} = \text{SiO}_2 + 4 \text{CH}_3\text{OH}$  and the aqueous phase of the resulting gel therefore contains approximately 10 volume% methanol. In the author's experience, the gelling time at room temperature usually takes no more than a day or two, but is a function of the composition of the aqueous

phase [5, 6]. The silica hydrogel produced from TMS provides a stable medium for the growth of crystals over a wide range of temperature (0-60°C) and a broad range of pH [1, 2, 5].

One of the strengths of crystal growth in gel media is the ability to control the composition of the aqueous phase that permeates the gel. The hydrolysis of TMS can be undertaken with dilute aqueous solutions - metal nitrates, chlorides or sulfates. Such solutions, although slightly diluted with the methanol that results from the hydrolysis reaction, then comprise the aqueous phase of the gel.

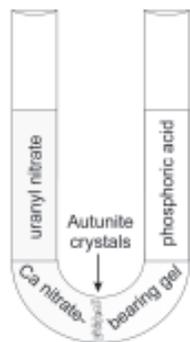
In the example shown at left, a gel has been formed in the presence of aqueous calcium nitrate. A U-shaped tube is used to provide two reservoirs for aqueous solutions of the reagents uranyl nitrate and phosphoric acid. The acidic reagents diffuse into the Ca-bearing gel, and where they meet, the highly insoluble compound autunite,  $\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{11}$ , crystallizes. The crystals are suspended in the gel medium and growth takes place mainly by diffusion, leading to crystals with a very high degree of perfection (low dislocation density).

Concentration gradients result from the differences between the initial compositions of the gel and the two reservoirs. In this example, uranyl nitrate and phosphoric acid diffuse into the gel, and the initial nucleation and growth of the autunite crystals takes place at significantly lower concentrations of these reagents than exists in the reservoirs. At the same time, the calcium nitrate (and methanol) diffuses out of the gel and into the two reservoirs.

The compatibility of reagents must be considered when growing crystals in gels in order to avoid crystallization of unwanted phases. For example, if the above experiment is duplicated using an aqueous solution of lead (II) nitrate instead of calcium nitrate, the compound  $\text{PbHPO}_4$  crystallizes at the boundary between the Pb-bearing gel and the phosphoric acid, and the experiment fails to grow prazhevalskite,  $\text{Pb}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_4$ . A more successful tactic is to place the lead (II) nitrate in with the uranyl nitrate. The Pb and U then diffuse at the same rate through the silica hydrogel, and crystallization takes place upon encountering the phosphoric acid that diffuses in from the other reservoir.

The growth of crystals in gel media is dominated by diffusion and is therefore relatively slow. In the wide variety of uranyl phosphate (and arsenate) hydrates investigated by the author, crystals of reasonable size (100 – 500  $\mu\text{m}$  maximum dimension) took from between 2 weeks to 6 months to grow from solutions whose initial concentrations were in the range of 0.1 – 1.0 mol/L.

Crystal growth can be slowed by using less concentrated solutions, a longer gel path between reservoirs, and more effectively by using denser gel media.



However, if the gel density is very high, two significant problems can occur: 1) diffusion-limited morphologies such as skeletal, dendritic and branched crystal forms may become dominant [7], and 2) the gel may not be able to be removed from the U-shaped tube without damage to the contained crystals.

In addition to controlling the cation-composition of phases through the aqueous phases in the two reservoirs and the gel, it appears that in some chemical systems, the hydration state of the crystals can be influenced through control of the bulk dielectric constant of the system. For instance, metatorbernite,  $\text{Cu}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_8$ , is the result of a gel-growth experiment at room temperature in which the reagents are uranyl nitrate, cupric nitrate, and phosphoric acid. If the same system is refrigerated at 5°C, torbernite,  $\text{Cu}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{12}$ , is the phase that crystallizes. The dielectric constant of water increases with the decrease in temperature, and may cause a change in the solvation of the ions in solution and thus the hydration state of the crystal products. Similarly, in the system U-Ni-P, the compound  $\text{Ni}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{10}$  is the product when the initial reagents are dissolved in a 1:1 methanol:water mixture. The higher hydrate  $\text{Ni}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{12}$  is the product in the nearly methanol-free version of the experiment. As the dielectric constant of methanol is much lower than that of water, a change in ionic solvation can be expected, and may help to explain the difference in the hydration state of the crystal products. **Note:** uranyl acetate should not be used in the presence of methanol, as the uranium tends to undergo photo-reduction, producing an exceedingly fine-grained black precipitate.

Crystallization in gels is highly suited to the growth of low solubility and low thermal stability compounds. An upcoming application may be crystallization of uranyl vanadates such as tyuyamunite,  $\text{Ca}[(\text{UO}_2)_2\text{V}_2\text{O}_8](\text{H}_2\text{O})_{5-8}$ , and hydrated carnotite,  $\text{K}_2[(\text{UO}_2)_2\text{V}_2\text{O}_8](\text{H}_2\text{O})_{1-3}$ .

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