Inorganica Chimica Acta, *109* (1985) 51–53

The Monazite and Xenotime Micro-crystallites formed by Lanthanides in Phosphotungstate Glasses

H. MACK, R. REISFELD

Department of Inorganic Chemistry, Hebrew University, 91904 Jerusalem, Israel

and C. K. JØRGENSEN

Département de Chimie minérale, analytique et appliquée, Université de Genève, CH 1211 Geneva 4, Switzerland

Received July 23, 1984

Abstract

Glasses consisting of sodium phosphate and more than 70 weight % tungsten trioxide, when doped with lanthanides, undergo phase separations producing monazite-type $PrPO_4$ and $EuPO_4$ or xenotime-type $HoPO_4$ and $TmPO_4$ identified with X-ray diffraction powder-diagrams, and compared with previous studies of luminescence, and nucleation of silicate glasses induced by chromium(III).

Introduction

Though monomeric orthophosphate PO_4^{-3} is a strong base readily protonated in aqueous solution, several trivalent and quadrivalent elements form extremely insoluble phosphates frequently known as minerals in alluvial deposits. Yttrium and the lanthanides form two types of binary phosphates, the monoclinic monazite and the tetragonal xenotime. The crystal structure [1–5] of mineral and synthetic monazite is slightly controversial, insofar as the exact positions of the oxygen nuclei are concerned. In $CePO_4$, the nine Ce–O distances are broadly scattered between 2.43 and 2.63 Å [2] or between 2.445 and 2.779 Å [5]. On the other hand, xenotime is isotypic with zircon $ZrSiO_4$ and has eight M–O distances in two sets of four [6] with a relatively high site symmetry D_{2d} which has played a certain role in the study of narrow absorption bands [7] of lanthanides incorporated in xenotime-type crystals [8, 9] among which the best known is $Eu_xY_{1-x}VO_4$ providing the red cathodoluminescence in colour television.

It is surprising that lanthanides in $LnPO_4$ choose either [6, 10] monazite (Ln = La to Gd; and Tb below 1000 °C) or xenotime (Ln = Dy to Lu; as well as Tb above 1000 °C) type, when the two minerals only discriminate to a moderate extent between rare earths with larger or smaller ionic radii. The absence of dimorphism is more striking when compared [11] with the hexagonal A-type, low-symmetry B-type and cubic C-type (with two Ln sites) of Ln_2O_3 and the polymorphism of many mixed oxides of lanthanides with zirconium(IV) and thorium(IV) frequently involving superstructures or disordered forms of the fluorite type [12–14]. The sharp demarcation line between $GdPO_4$ and $TbPO_4$ has nothing to do with a half-filled 4f shell, but is rather connected with the relative size of Ln^{+3} and XO_4^{-3} as seen from the arsenates [10] where the dividing line is between $NdAsO_4$ and $SmAsO_4$. The larger orthovanadates are known [9, 10] in xenotime-type $PrVO_4$ to $LuVO_4$ whereas $LaVO_4$ is a monazite. The mineral fergusonite of idealized composition $Ln(NbO_4)_{1-x}(TaO_4)_x$ is generally amorphous metamict (probably due to α-radioactivity of incorporated uranium(IV) and thorium) but certain crystalline samples show xenotime-type, as one would expect from the large size of the (infrequent) tetrahedral niobate and tantalate anions. In this connection, it may be noted that thorite $ThSiO_4$ usually crystallizes in the xenotime type like zircon, but that a monoclinic modification huttonite [15] isotypic with monazite also occurs.

The results reported here derive from a study of the nucleation of $LnPO_4$ from a long series of phosphotungstate glasses containing small amounts of lanthanides and/or uranyl ions [16–18]. The name of these glasses does not refer to heteropoly-anions [19] but to a molten mixture of a large amount of tungstates and a smaller amount of phosphates of relatively big colourless cations. However, since only $LnPO_4$ is seen in the micro-crystallites (and not the otherwise quite stable and water-insoluble $Ln_2(WO_4)_3$ or scheelite-type $NaLn(WO_4)_2$ [9]) the tungstate may still be tied up in the glass in some kind of poly-anion in view of the phosphate concentration well in excess of that needed to form $PW_{12}O_{40}^{-3}$. Such phosphotungstate glasses were previously studied [20], made from roughly

0020-1693/85/$3.30

TABLE I. The *d* Values (Å) of the Strongest Powder-Diagram Diffraction Lines arranged according to Decreasing Intensities. The Detailed Composition of the Glasses is given at the Beginning of the Section 'Results and Conclusions'.

Pr(III) + uranyl	3.08	2.85	3.29	4.16	1.87	1.96	4.65
monazite-$PrPO_4$	3.09	2.86	3.30	4.17	1.87	1.96	4.66
Eu(III), uranyl-free	3.04	2.81	3.24	4.11	1.92	2.56	4.58
Eu(III) + uranyl	3.04	2.82	3.24	4.11	1.92	2.57	4.60
monazite-$EuPO_4$	3.02	2.81	3.24	4.11	1.92	2.56	4.59
Ho(III) + uranyl	3.45	2.55	4.53	1.77	2.14	2.43	–
xenotime-$HoPO_4$	3.45	2.56	4.54	1.77	2.15	2.43	–
Tm(III) + uranyl	3.41	2.53	4.46	1.75	–	–	–
xenotime-$TmPO_4$	3.42	2.55	4.52	1.75	–	–	–

3 WO_3:1 $Na_4P_2O_7$ and doped with about one percent europium(III). It was shown that the precipitation of extremely finely dispersed micro-crystallites is a very sensitive function of the ratio W:P and in our more extended experiments [16] samples containing less than 70 weight percent WO_3 always remained homogeneous and limpid. In the case of glasses with precipitated $EuPO_4$, the very sharp emission lines at liquid helium temperature [18] coincide with those of monazite-type crystalline $EuPO_4$.

Experimental

Mixtures of WO_3 (B.D.H.), Na_2HPO_4, H_2O (Mallinckrodt), NaH_2PO_4 (Hopkin and Williams) and 99.9% pure Pr_2O_3, Eu_2O_3, Ho_2O_3 and Tm_2O_3 (all from Mallinckrodt), $UO_2(CH_3CO_2)_2$, 2 H_2O (B.D.H.), p.a. Li_2CO_3 and K_2CO_3 (Baker) were dried at 120 ℃ overnight, mixed in a mullite vibrator ball mill, and made molten at around 1000 ℃ in 90 minutes (shaken occasionally) in a platinum crucible. However, high concentrations of rare earths needed heating at a slightly higher temperature for 3 h. The liquid was poured on a tile inside a copper ring of 16 mm diameter and pressed into 1 mm thickness with another tile plate.

The weight percent WO_3 was varied [16] between 50 and 80, but most samples were in the interval 65 to 75. Between 60 and 70, it is easy to dissolve 4 to 5 weight % rare earths and still obtain a limpid glass. The other samples (containing micro-crystallites) are milky and uniformly translucent.

Microscopic photographs of the light-scattering samples show irregularly shaped crystallites and chunks with linear dimensions typically 10 μ in the case of the monazite-type, and elongated xenotime tetragonal prisms, some 20 μ long and 3 μ thick. Electron probe microanalysis was performed, using scanning and X-ray fluorescence techniques, showing tungsten to be practically absent.

X-ray powder diagrams were obtained with a Philips diffractometer (Cu Kα 1.54178 Å, 40000 V, 20 mA, equipped with Tl-NaI scintillation detector) and standardized with the diffraction pattern of silicon.

Results and Discussion

Table I gives the *d* values (in Å) for the four to seven strongest powder-diagram lines of five phosphotungstate glasses containing microcrystallites and of the corresponding pure phosphates (from data in the JCPDS file for inorganic materials). Four glasses (called Ln(III) + uranyl in Table I) have the weight % composition 70 WO_3: 11.28 P_2O_5: 9.84 Na_2O: $4UO_2^{+2}$:$4Ln^{+3}$. The glass called 'Eu(III) uranyl-free' is $70WO_3$:$10.46P_2O_5$:$9.12Na_2O$:$9Eu^{+3}$. It is clear that all or nearly all the crystalline precipitate has monazite-type for the Pr(III) and Eu(III) glasses, and xenotime-type for the Ho(III) and Tm(III) glasses. Further on, it is seen on our diffraction curves that the light-scattering glasses do not contain perceptible amounts of the alternative $LnPO_4$ type. This behaviour of a single rare earth is in contrast with small amounts of Nd(III) or Eu(III) incorporated [9] in xenotime-type YPO_4.

The unit cell parameters must be quite similar (within 0.3%) for the monazite-type, when dispersed in glasses and in the stoichiometric compounds (to be compared with some 1.7% contraction from $PrPO_4$ to $EuPO_4$). The variation seems to be slightly larger in the cases involving the xenotime-type, the contraction from $HoPO_4$ to the Ho(III) glass being slightly smaller, and from $TmPO_4$ to the Tm(III) glass slightly larger, than the contraction (average 0.6% in the linear dimensions [10]) from crystalline $HoPO_4$ to $TmPO_4$. This variation may be compared with the fluorescence data [18] for $EuPO_4$ micro-crystallites showing the 'ligand field' separations of $^7F_1$ one percent larger than that of monazite-type $EuPO_4$, and the wave-number of the undivided state $^5D_0$ decreased by 0.006% in the micro-crystallites. This marginal effect might indicate a tiny compression of the internuclear distances in the latter case.

Starting with the asymptotic limit of molar composition 2.68 WO_3:1 P_2O_5:2Na_2O corresponding to 70 weight % WO_3, addition of either UO_2^{+2} or slightly more WO_3 enhances the tendency of any Ln(III) simultaneously added to precipitate as $LnPO_4$. The corresponding limit of 75 weight % WO_3 (strongly favouring $LnPO_4$ precipitation) has the molar composition 3.50 WO_3:1P_2O_5:2Na_2O. The simplest (but not unique) explanation for this behaviour is that an anion of stoichiometric ratio $W_4P_3O_{22}^{-5}$ (oligomers by no means excluded) maintains a buffer level of phosphate activity. $LnPO_4$ is soluble in this system much in the same way as Ln(III) forms pyrophosphate complexes $Ln(P_2O_7)_2^{-5}$ in aqueous solution. When UO_2^{+2} or WO_3 are added, the phosphate activity is decreased, and $LnPO_4$ starts to precipitate.

The nucleation of glasses when a crystalline compound supercedes its solubility is rather similar to the formation of minerals from a liquid phase. An interesting case [21, 22] is the influence of low concentrations of chromium(III) (of which the visible absorption spectrum is a suitable indicator) on a silicate melt with composition close to that of cordierite $Mg_2Al_4Si_5O_{18}$ where micro-crystallites of spinel-type $MgCr_2O_4$ are first formed. When the crystallization proceeds, the product is $Mg(Al_{1-x}Cr_x)_2O_4$ with x rapidly vanishing. Related phenomena are observed [23, 24] by the formation of limpid (the micro-crystallites being smaller than wave-length of violet light) glass ceramics containing two kinds of chromium(III) in the vitreous and crystalline microscopic phases. Such materials are of potential use for luminescent solar concentrators [25].

The combination of the X-ray powder-diagrams discussed here, highly resolved absorption, excitation and luminescence spectra [17, 18, 20] and microprobe analytical techniques [16] allows the use of lanthanides to elucidate the complex behaviour of phase separations in glasses.

Acknowledgements

We are grateful to Professor I. Mayer, Hebrew University, for helpful information about powder-diagrams.

The investigation was supported by the joint project (contract No. 80-1-09) of the U.S. Department of Energy and the Israeli Ministry of Energy. The study in Geneva was also assisted by grant No. 2.152.083 of the Swiss National Science Foundation.

References

1 R. C. L. Mooney, *J. Chem. Phys., 16,* 1003 (1948).
2 T. Ueda, *Mem. Coll. Sci., Univ. Kyoto, Ser. B20,* 227 (1953).
3 K. M. Ghouse, *Naturwissenschaften, 52,* 32 (1965).
4 J. J. Finney and N. Nagaraja Rao, *Am. Mineral., 52,* 13 (1967).
5 G. W. Beall, L. A. Boatner, D. F. Mullica and W. O. Milligan, *J. Inorg. Nucl. Chem., 43,* 101 (1981).
6 W. O. Milligan, D. F. Mullica, G. W. Beall and L. A. Boatner, *Inorg. Chim. Acta, 70,* 133 (1983).
7 R. Reisfeld and C. K. Jørgensen, 'Lasers and Excited States of Rare Earths', Springer-Verlag, Berlin, 1977.
8 D. Kuse and C. K. Jørgensen, *Chem. Phys. Lett., 1,* 314 (1967).
9 C. A. Morrison and R. P. Leavitt, in K. A. Gschneidner and L. Eyring (eds.), 'Handbook on the Physics and Chemistry of Rare Earths, Vol. 5', North-Holland, Amsterdam, 1982, p. 461.
10 H. Schwarz, *Z. Anorg. Chem., 323,* 44 (1963).
11 L. Eyring, in K. A. Gschneidner and L. Eyring (eds.), 'Handbook on the Physics and Chemistry of Rare Earths, Vol. 3', North-Holland, Amsterdam, 1979, p. 337.
12 C. K. Jørgensen and E. Rittershaus, *Mat. Fys. Medd. Dan Vid. Selskab (Copenhagen), 35,* No. 15 (1967).
13 C. K. Jørgensen, in K. A. Gschneidner and L. Eyring (eds.), 'Handbook on the Physics and Chemistry of Rare Earths, Vol. 3', North-Holland, Amsterdam, 1979, p. 111.
14 C. K. Jørgensen and R. Reisfeld, *Top. Curr. Chem., 100,* 127 (1982).
15 A. Pabst, *Nature, 166,* 157; 590 (1950).
16 H. Mack, *Ph.D. Thesis,* Hebrew University, Jerusalem, 1981.
17 H. Mack. G. Boulon and R. Reisfeld, *J. Lumin., 24,* 111 (1981).
18 F. Durville, G. Boulon, R. Reisfeld, H. Mack and C. K. Jørgensen, *Chem. Phys. Lett., 102,* 393 (1983).
19 M. T. Pope, 'Heteropoly and Isopoly Oxometalates', Springer-Verlag, Berlin, 1983.
20 R. Reisfeld, H. Mack, A. Eisenberg and Y. Eckstein, *J. Electrochem. Soc., 122,* 273 (1975).
21 F. Durville, *Ph.D. Thesis,* No. 1436, Université I, Lyon, 1984.
22 F. Durville, B. Champagnon, E. Duval, G. Boulon, F. Gaume and A. F. Wright, *Phys. Chem. Glasses,* submitted.
23 R. Reisfeld, A. Kisilev, E. Greenberg, A. Buch and M. Ish-Shalom, *Chem. Phys. Lett., 104,* 153 (1984).
24 A. Kisilev, R. Reisfeld, E. Greenberg. A. Buch and M. Ish-Shalom, *Chem. Phys. Lett., 105,* 405 (1984).
25 R. Reisfeld and C. K. Jørgensen, *Struct. Bonding, 49,* 1 (1982).