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Glassy and Crystalline Phases in the PbO–V_2O_5 System

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Despite the relatively simple composition, the system PbO–V_2O_5 presents an interesting behavior due to the formation of a number of stable and metastable crystalline phases, depending on its composition and the cooling rate of the melt. By means of single-crystal X-ray diffraction, optical, electron microscopy, and thermal analysis, we were able to identify the resulting crystals and to correlate their structure with laboratory conditions. Moreover, the study of this correlation showed that there is one lead metavanadate which is stable, despite the commonly accepted phase diagram. © 1985 Academic Press, Inc.

1. Introduction

New metastable phases in the equimolar PbO–V_2O_5 system were obtained by Baiocchi *et al.* (*1*). In the same paper, the authors reported that lead metavanadate PbV_2O_6(I) (*2*) is a stable phase despite the commonly accepted phase diagram (*3*).

On the basis of these investigations, we have extended the study to systems with a higher V_2O_5/PbO molar ratio in order to determine if an excess of vanadium influences the devitrification of the glassy system. The preliminary results have suggested restudy of the equimolar system, in order to define the stoichiometry of the metastable crystalline phases (*1*). The key to the interpretation of the data has been the preparation of crystals suitable for single-crystal X-ray diffraction studies and the production of nearly pure samples of the metastable phases.

2. Experimental Procedure

Various mixtures of vanadium oxide (V_2O_5) and lead oxide (PbO) were melted in an electrically heated furnace and were kept at 650°C for 2 hr to ensure a good homogeneous melt. The melts were quenched in a liquid-nitrogen-cooled vessel, on a stainless-steel plate (melt MM2), and on a copper plate (melt MM1). Powder XRD analysis was carried out on quenched and heat-treated samples. Single-cystal data were collected by a Philips PW 1100 diffractometer fitted with a graphite monochromator. A Linseis L62 thermal analysis appa-

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ratus was used to collect DTA data under an air atmosphere in the range 20–520°C.

3. Results and Discussion

3.1. Phase Identification

Table I shows the cooling behavior of lead vanadate melts. All batches quenched in liquid-nitrogen-cooled graphite vessels, give rise to a homogeneous vitreous phase, whose composition was the same as that of the starting mixture.

Lower quenching rates led to inhomogeneous samples in which the glassy phases contain one or more crystalline vanadates. The phenomenon seems due to the low heat transfer rate from the sample (Fig. 1).

Slow cooling of the melts produce crystals of the stable phase of lead metavanadate PbV_2O_6(I), which are mixed with crystalline V_2O_5 for a V_2O_5/PbO molar ratio greater than 1.

In equimolar PbO–V_2O_5, the crystalline phases embedded in the glassy matrix obtained by quenching on copper or steel plates were identified by Baiocchi *et al.* (*1*) as lead pyrovanadates using electron microprobe analysis. A more accurate electron and optical microscope analysis suggested the existence of two different crystalline phases. By breaking the samples, we are able to isolate crystals suitable for single-crystal X-ray analysis. Crystals obtained from MM1 were identified as chervetite ($Pb_2V_2O_7$) (*4*) and a modification of lead metavanadate (PbV_2O_6(III)) (*5*). Chervetite was formed in MM2, together with another structural modification of lead metavanadate (PbV_2O_6(II)) (*6*). The crystallographic data of these two polymorphs are reported in Table II.

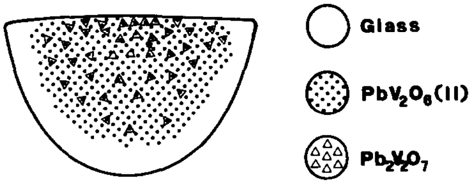

FIG. 1. Phase separation in a MM2 sample quenched in a stainless-steel vessel.

Increasing the V_2O_5/PbO batch molar ratio to about 1.2 leads to separation of

TABLE I

COOLING BEHAVIOR OF LEAD VANADATE MELTS

Molar ratio V_2O_5/PbO		Cooling mode	Products
1.0	Melt	Graphite + N_2(l)	Glass
		Copper	Glass + PbV_2O_6(III) + $Pb_2V_2O_7$
		Steel	Glass + PbV_2O_6(II) + $Pb_2V_2O_7$
		Slow cooling	PbV_2O_6(I)
1.2	Melt	Graphite + N_2(l)	Glass
		Copper	Glass + PbV_2O_6(III)
		Steel	Glass + PbV_2O_6(II)
		Slow cooling	PbV_2O_6(I) + V_2O_5
1.4–2.0	Melt	Graphite + N_2(l)	Glass
		Copper	Glass + Bronze ($Pb_xV_2O_5$)
		Steel	Glass + Bronze + PbV_2O_6(III) + PbV_2O_6(II)
		Slow cooling	PbV_2O_6(I) + V_2O_5

TABLE II

CRYSTALLOGRAPHIC DATA OF METASTABLE LEAD METAVANADATES[a]

Compound	Space Group	Z	a	b	c	β
PbV_2O_6(II)	$C2/m$	4	15.525(2)	3.6960(6)	9.436(4)	110.44(1)
PbV_2O_6(III)	$C222$	6	8.273(2)	12.422(2)	7.685(1)	

[a] Lattice constants in Ångstroms and degrees; e.s.d. in parentheses.

the crystalline metavanadates only (PbV_2O_6(III) and PbV_2O_6(II)). An excess of V_2O_5 prevents the formation of the chervetite. For greater V_2O_5/PbO molar ratios the quenching on copper plates separates from the glassy phase a crystalline vanadium bronze $Pb_xV_2O_5$ (monoclinic, space group $C2/m$, $a = 15.337(4)$, $b = 3.597(3)$, $c = 10.049(2)$ Å, $\beta = 109.5(1)°$, $Z = 6$) with a structure comparable with that of the β-$Pb_xV_2O_5$ phase (*7*). This structure, existing for $0.15 < x < 0.33$, consists of a V_2O_5 framework which contains tunnels parallel to the b axis. Lead atoms are interspersed in these tunnels and partially occupy the $4i$ site on the mirror plane. The upper composition limit $x = 0.33$ corresponds to a half-occupation of this site. Only one of the two equivalent positions on the same mirror plane is occupied, leading to Pb–Pb distances in excess of 3.6 Å. A further increase of the lead content is forbidden by steric effects because of the short distance (2.6 Å) between two adjacent positions on the same plane. For $0.01 < x < 0.15$ it was found (*7*) that the system disproportionates into α- and β-$Pb_xV_2O_5$. This second phase is characterized by $x < 0.01$.

The measured lattice parameters of the $Pb_xV_2O_5$ bronze are significantly smaller than those for the β-phase, suggesting a lower lead content. A structure analysis performed, using 123 observed reflections collected from a small crystal, confirmed a lower occupation of the $4i$ site, leading to the formula $Pb_{0.09}V_2O_5$ (site occupation factor 0.07(1) for $R = 0.11$).

When quenching the same composition on a steel plate, the separation of $Pb_xV_2O_5$ from the glassy phase is accompanied by the two phases PbV_2O_6(III) and PbV_2O_6(II).

3.2. *Thermal Behavior*

The thermal behavior of the equimolar PbO–V_2O_5 system was previously investigated by Baiocchi *et al.* (*1*), who interpreted the DTA patterns in terms of a sequence of transitions from the vitreous high-energy state to a crystalline, low-energy, stable metavanadate. The preparation of PbV_2O_6(II) in nearly pure form, allowed us to assign all the observed peaks. The crystalline phases existing in the samples during the thermal experiments were identified by stopping the temperature rise and carrying out XRD powder spectra. Figure 2 shows the thermal evolution of typical samples.

All the glasses with equimolar composition devitrify at temperatures of roughly 300°C into PbV_2O_6(III), which transforms into PbV_2O_6(I) at 386°C. PbV_2O_6(II) is stable up to 404°C, when it transforms into PbV_2O_6(I).

Samples from MM1 and MM2 exhibit two common peaks at about 300 and 384°C due, respectively, to the devitrification of the glass embedded in the crystalline material, producing the PbV_2O_6(III) phase and the $PbV_2O_6(III) \rightarrow PbV_2O_6(I)$ phase transition. Samples containing the PbV_2O_6(II) phase obtained from MM2 show, in addition, the $PbV_2O_6(II) \rightarrow PbV_2O_6(I)$ transition peak at 404°C. No evidence is found for a

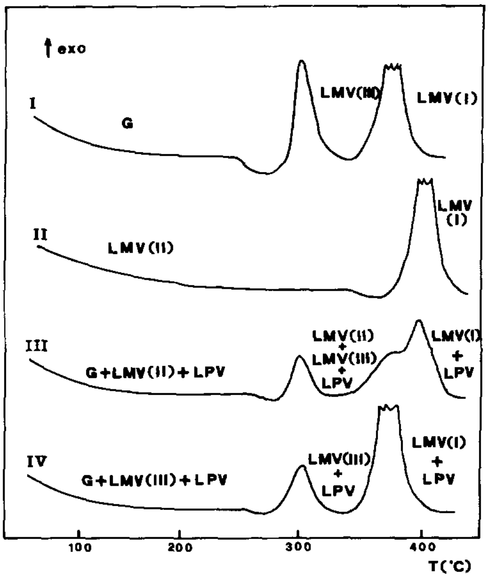

FIG. 2. DTA patterns of (I) equimolar glass; (II) crystalline PbV_2O_6(II); (III) almost fully crystallized MM2 zone; (IV) almost fully crystallized MM1 zone. LMV, lead metavanadate; LPV, lead pyrovanadate; G, glass.

PbV_2O_6(III) → PbV_2O_6(II) transformation. XRD analysis performed on samples containing both phases showed the presence of PbV_2O_6(I) just above the peak at 384°C. In this manner, all the peaks are assigned to transition involving glass and/or metavanadate. $Pb_2V_2O_7$ remains unaffected during the thermal analysis; only after prolonged heating at 450°C of MM1 and MM2 does it transform to PbV_2O_6(I) by reaction with the remaining V_2O_5.

Thermodynamic data, XRD analysis, and the preparation behavior confirm that Pb V_2O_6(I) is the only stable lead metavanadate. The other two forms, PbV_2O_6(II) and PbV_2O_6(III), are metastable, evolving into the stable one at 404 and 384°C, respectively.

Glasses with V_2O_5/PbO molar ratio of 1.4 and 2 devitrify, giving rise to the PbV_2O_6(I) phase, at temperatures depending on the composition (Fig. 3). The transformation G → PbV_2O_6(I) + V_2O_5 (g) is observed at 283 and 261°C for the glasses with V_2O_5/PbO molar ratio of 1.4 and 2. The second peak observed at 384 and 362°C is due to the devitrification of vitreous V_2O_5. DTA patterns recorded for polycrystalline samples obtained by quenching V_2O_5-rich melts on steel and copper plates are complex even when they are reducible to the patterns of the single components. It must be noted that the bronze $Pb_xV_2O_5$ remains stable during the heat treatment up to the melting point of the system.

4. Conclusion

Phase diagrams reported by Amadori (*3*) and Shimoira *et al.* (*8*) indicate that an eutectic is found in the $PbO–V_2O_5$ system at a 1:1 composition. Jordan and Calvo (*2*) stated that crystals of composition PbV_2O_6 could be obtained by slow cooling of a $PbO–V_2O_5$ melt and suggested that those crystals are a stable crystalline phase. This suggestion is confirmed by our work. In fact, we obtained three crystalline phases of composition PbV_2O_6. This high number of crystalline phases with the same compo-

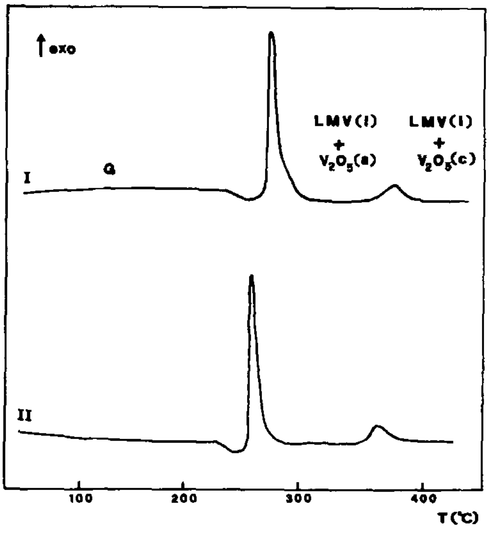

FIG. 3. DTA patterns of vanadium-rich glasses: (I) V_2O_5/PbO, 1.4:1; (II) V_2O_5/PbO, 2:1.

sition is unusual for an eutectic point. Considering that PbV_2O_6(II) and PbV_2O_6(III) transform into the stable PbV_2O_6(I) and that the latter is not affected by heat treatment below its melting point, the hypothesis of the existence of a stable phase of composition PbV_2O_6 is confirmed. Moreover, enrichment or deficiency of V_2O_5 in the melt always gives rise to PbV_2O_6, together with a vanadium-rich bronze $Pb_xV_2O_5$, or a lead-rich $Pb_2V_2O_7$ compound, respectively.

The formation of $Pb_xV_2O_5$ is proof for the presence of V^{4+} in the melt, which is responsible for the electrical conductivity of these materials. It must be pointed out that the stoichiometry of the bronze obtained by quenching the V_2O_5-rich melt is unusual. These bronzes contain lead in a quantity smaller than that found in the corresponding bronze prepared by reaction of V_2O_5, VO_2, and PbO. The composition seems to depend on the concentration of V^{4+} in the melt and on the high cooling rate, which allows the freezing of the system.

Another significant feature is the role of the V_2O_5/PbO molar ratio in the devitrification process. Glasses with approximately equimolar composition devitrify into Pb V_2O_6(III); an increase of V_2O_5 changes the devitrification product into PbV_2O_6(I). This is probably due to a modification in the glass structure, with an increase in the V_2O_5 content. Structural studies on PbV_2O_6(III) (*5*) show that its structure consists of infinitely extended single chains of linked VO_4 tetrahedra with interspersed Pb atoms. On the basis of IR spectra (*1*) it is speculated that this structure is preserved, with introduction of disorder in the glass. It is likely that additional V_2O_5 favors the formation of more complex chains with a consequent devitrification into a crystalline phase having a more complex arrangement of VO_6 octahedra. The V_2O_5/PbO molar ratio 1.2 seems to be on the borderline between the formation of the PbO-rich phase $Pb_2V_2O_7$ and the V_2O_5-rich phase $Pb_xV_2O_5$.

Acknowledgments

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