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Properties of the glasses prepared by rapid quenching in the V_2O_5–MO(M = Mg, Ca and Ba) system

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Rapidly quenched glasses in the V_2O_5–MO (M = Mg, Ca and Ba) systems have been prepared by a twin-roller technique. Glasses up to 40 mol% MgO and 50 mol% CaO or BaO were obtained. No metastable phase was observed in the crystallization processes. From the infrared spectral data for the glasses, the structural change of the glasses are discussed. The electrical conductivity of the glasses decreased with increasing MO content, and the electrical behaviour of the glasses has been related to the structural change of the glasses.

1. Introduction

Vanadate glasses containing other glass-forming oxides such as P_2O_5 [1], GeO_2 [2], with a wide composition range, or glass modifying oxide such as BaO [3], PbO [4], with a narrow composition range have been prepared by normal quenching of the melt. In addition, some vanadate glasses show semiconductive properties based on the electron hopping between V^{5+} and V^{4+} ions. Sarjent and Roy applied a rapid-quenching technique to oxide systems [5]. This method has been used to prepare the glasses in the new system or those with a wider composition range than those by the conventional method.

In the binary systems of V_2O_5 and alkaline earth metal oxide (Mg, Ca and Ba), MV_2O_6 (metavanadate), $M_2V_2O_7$ (pyrovanadate) and $M_3V_2O_8$ (orthovanadate) were commonly found to form. Dimitriev *et al.* carried out glass formation in the V_2O_5–MO systems by rapid quenching, and reported a glass formation region of 0–40 mol% MO in each system [6]. Further, they measured infrared (IR) absorption spectra of the rapidly quenched glasses in these systems [7]. However, other properties of these rapidly quenched glasses were not reported.

In the present work, systematic studies on the glass formation by rapid quenching in the V_2O_5–alkaline earth metal oxide (MgO, CaO and BaO) and the properties of these glasses, were conducted. The effects of the kind of alkaline earth metal on the glass-formation region and the IR absorption and electrical conductivity of the glasses were investigated.

2. Experimental procedure

The starting powders were prepared by firing the mixtures of vanadium pentaoxide and magnesium, calcium or barium carbonate at 500–1000 °C in air. Three common compounds (MV_2O_6, $M_2V_2O_7$ and $M_3V_2O_8$) formed by solid state reaction. In addition, $Ca_7V_4O_{17}$ [8] was confirmed to form. The reacted powders were pressed into rod shape (5 mm × 5 mm × 30 mm) and sintered in air. The apparatus used for the rapid-quenching treatment consisted of a thermal image furnace and a metallic twin roller (50 mm diameter) [9]. The sintered rod sample was placed in the furnace and melted from the lower end. The molten droplets fell between the counter-rotating rollers at 3000 r.p.m. to be quenched. The prepared films were about 20 μm thick.

The X-ray diffraction method was used to identify the glassy and/or crystalline phases in the quenched films. Differential thermal analysis (DTA) and thermogravimetry (TG) curves were measured in air at a heating rate of 10 °C min^{-1} in order to investigate the thermal behaviour of the quenched films. IR absorption spectra were obtained between 2000 and 400 cm^{-1} by dispersing the ground film into KBr pellet. Electrical conductivity of the quenched films was measured in air between 25 and 200 °C using evaporated gold as electrodes, which makes good ohmic contacts to vanadate glasses [10].

3. Results and discussion

3.1. Glass formation and crystallization behaviour

The composition of the samples is indicated by x, the molar fraction of MO in the $(1-x)$ V_2O_5–xMO system. The colour of the as-quenched films changed from dark brown for $x = 0$ to lighter brown with increasing x in all three systems. Table I shows the compositions and the phases identified by X-ray diffraction in the sample before and after quenching. In the V_2O_5–MgO system, the glass-formation region ranged from $x = 0$–0.40 and the quenched film of $x = 0.50$ contained a small amount of crystalline $Mg_2V_2O_7$. Because MgV_2O_6 ($x = 0.50$) melted incongruently to form liquid and $Mg_2V_2O_7$ [11], $Mg_2V_2O_7$ formed during quenching. The as-quenched films of

TABLE I Compositions, phases existing in the samples before and after quenching, and crystallization processes of the quenched sample in the $(1-x)\,V_2O_5$–xMO (M = Mg, Ca and Ba) system

x	Phase before quenching	Phase after quenching	Phase transition sequence[a]
0	V_2O_5	Glass	(210) V_2O_5
M = Mg			
0.20	$V_2O_5+MgV_2O_6$	Glass	(313) V_2O_5 + glass (343) $V_2O_5+MgV_2O_6$
0.40	$V_2O_5+MgV_2O_6$	Glass	(368) $V_2O_5+MgV_2O_6$
0.50	MgV_2O_6	Glass + $Mg_2V_2O_7$	(380) MgV_2O_6
M = Ca			
0.20	$V_2O_5+CaV_2O_6$	Glass	(291) $V_2O_5+CaV_2O_6$
0.40	$V_2O_5+CaV_2O_6$	Glass	(329) $V_2O_5+CaV_2O_6$
0.50	CaV_2O_6	Glass	(388) CaV_2O_6
0.60	$CaV_2O_6+Ca_2V_2O_7$	Glass + $Ca_2V_2O_7$	(408) $CaV_2O_6+Ca_2V_2O_7$
M = Ba			
0.20	$V_2O_5+BaV_2O_6$	Glass	(273) $V_2O_5+BaV_2O_6$
0.40	$V_2O_5+BaV_2O_6$	Glass	(349) $V_2O_5+BaV_2O_6$
0.50	BaV_2O_6	Glass	(392) BaV_2O_6
0.60	$BaV_2O_6+Ba_2V_2O_7$	Glass + $Ba_2V_2O_7$	(370) $BaV_2O_6+Ba_2V_2O_7$

[a] ( ) indicates transition temperature (°C).

$x = 0.40$ and 0.50 showed strong hygroscopicity. However, in the V_2O_5–CaO and V_2O_5–BaO systems, the glass-formation region was wider and ranged to $x = 0.50$. The quenched films of $x = 0.60$ in both systems contained crystalline $M_2V_2O_7$. The difference in the glass-formation region between MgO and other two oxides is attributed to that in the ionic radii of these alkaline earth metals which act as glass modifiers. Magnesium usually shows the coordination number of 6; on the other hand, calcium and barium prefer that of 8 or 12.

No weight change, associated with the oxidation or reduction of the vanadium ion, was detected for the as-quenched samples in the TG measurements. These results suggest that the reduction of the V^{5+} ion during melting and quenching took place to a very small extent. Fig. 1 shows the DTA curves of the as-quenched glasses. All the glasses except for the V_2O_5 glass ($x = 0$) showed a glass transition before the sharp exothermal peak by the first crystallization. The first crystallization temperature of the glasses rose with the increase of x in all three systems.

The crystallization processes of the quenched glasses are shown on the right-hand side of Table I. The glass of $x = 0$ directly crystallized to V_2O_5 at 210 °C. In the V_2O_5–MgO system, V_2O_5 firstly formed and then MgV_2O_6 appeared in the glass of $x = 0.20$. Both V_2O_5 and MgV_2O_6 crystallized at the same time at 368 °C in the glass of $x = 0.40$. In the other two systems, MV_2O_6 formed, associated with V_2O_5, in the first crystallization process in the glasses of $x = 0.20$ and 0.40. Only MV_2O_6 appeared in the glass of $x = 0.50$. No metastable phase was found in the crystallization process for the quenched glasses in all the three systems.

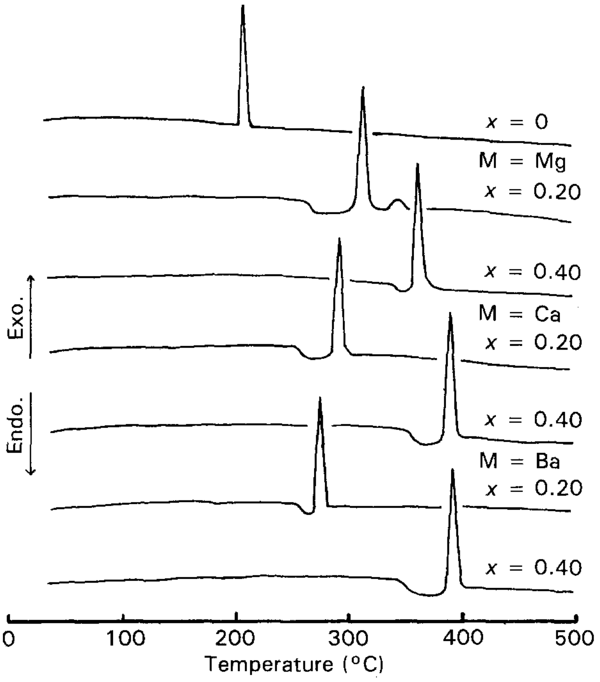

Figure 1 DTA curves of the as-quenched glasses in the $(1-x)$-V_2O_5–xMO (M = Mg, Ca and Ba) systems.

3.2. IR absorption of quenched glasses

IR spectrometry was used for structural studies of glasses. In the vanadate systems, characteristic vibration bands based on VO_n polyhedra exist between 1100 and 700 cm^{-1} for both crystalline and glassy phases. In general, glasses show a much broader absorption band than the corresponding crystalline phases. In all three systems, the spectra had the lowest absorption region around 1100 cm^{-1}. The location shifted towards the high wave number side with increasing MgO content, but shifted towards the low wave number side with the increasing BaO content. In the case of CaO, the location remained almost unchanged.

The IR absorption spectra for the glasses in the V_2O_5–MgO system are shown in Fig. 2. The V_2O_5 glass had one separated absorption band at 1020 cm^{-1}. This band was very sharp for the crystalline V_2O_5 and assigned to the stretching mode of one short V–O bond (0.158 nm) in the VO_5 polyhedra

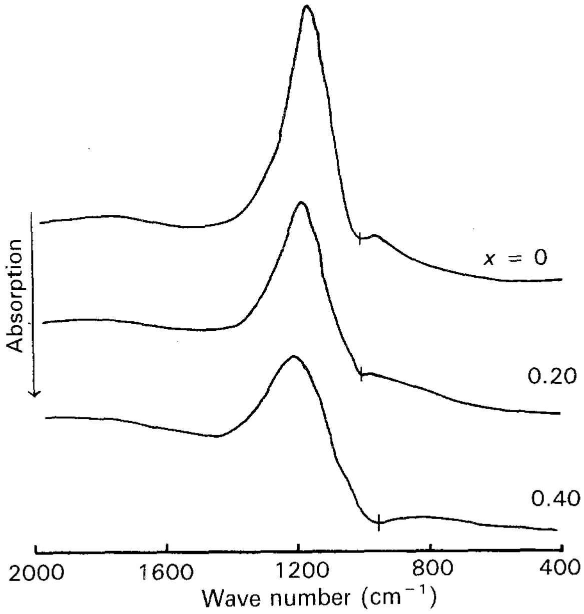

Figure 2 IR absorption spectra of the as-quenched glasses in the V_2O_5–MgO system.

which constructed the layer structure of V_2O_5 [7, 12, 13]. This result shows that the VO_5 polyhedra with one short bond persisted in the V_2O_5 glass. The band at 1020 cm^{-1} became weaker for the glass of $x = 0.20$. Instead, a new band at 950 cm^{-1} appeared for the glass of $x = 0.40$. This band was almost absent for the crystalline MgV_2O_6 which consisted of the VO_5 polyhedra without short bonds, unlike the crystalline V_2O_5, and showed two main bands at 890 and 690 cm^{-1}. The band at 950 cm^{-1} for the glass of $x = 0.40$ is thought to be the stretching of the shorter V–O bond in the VO_5 polyhedra than the shortest V–O bond of 0.167 nm in the crystalline MgV_2O_6 [14].

The IR absorption spectra for the glasses in the V_2O_5–CaO system are shown in Fig. 3. As shown in the case of the V_2O_5–MgO system, the band at 1020 cm^{-1} remained for the glass of $x = 0.20$. Further increase of x to 0.40 and 0.50 caused a new band at 950 cm^{-1}. The crystalline CaV_2O_6 had one short V–O bond of 0.161 nm in the VO_5 polyhedra [15] and showed three main bands 960, 840 and 560 cm^{-1}. The band at 950 cm^{-1} for the glasses is assigned to the stretching of the short V–O bond in the VO_5 polyhedra constructing the glass network structure, which has the coordination polyhedra around the vanadium ion similar to those in the crystalline CaV_2O_6.

The IR spectra for the glasses in the V_2O_5–BaO system are shown in Fig. 4. The isolated band at 1020 cm^{-1} was also observed for the glass of $x = 0.20$ in this system. A new band appeared at 900 cm^{-1} for the glass of $x = 0.40$ and 0.50. The crystalline BaV_2O_6 showed four large bands at 950, 900, 840 and 680 cm^{-1}. The band at 900 cm^{-1} for the glasses probably corresponds to that at 900 cm^{-1} in the crystalline state. As no detailed structural study on the crystalline BaV_2O_6 has been reported, further discussion of the coordination around the vanadium ion in the glassy state is difficult.

In all three systems, M^{2+} ions act as glass modifiers located between the glass network frame, and change the glass structure from that constructed by the VO_5 polyhedra with one shorter V–O bond as in the crystalline V_2O_5, to that based on the VO_5 polyhedra with longer V–O bonds, as in the crystalline metavanadates. The location of the absorption bands depends mainly on the ionic radii of M^{2+} ions.

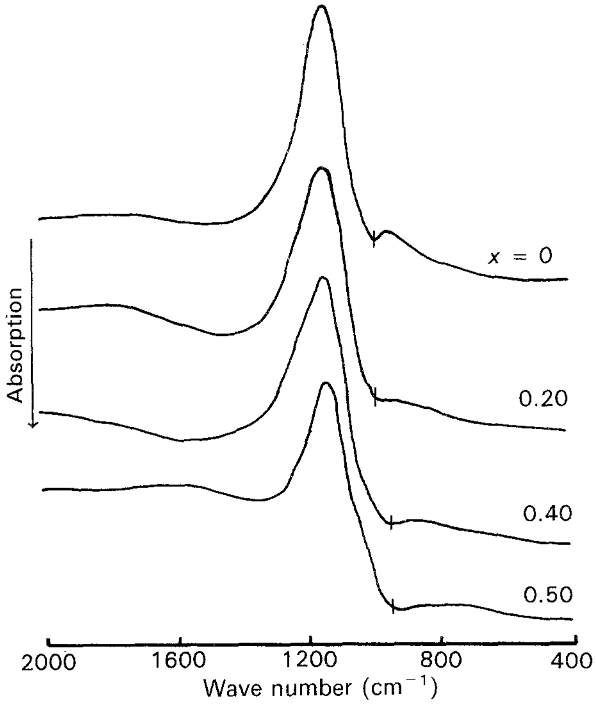

Figure 3 IR absorption spectra of the as-quenched glasses in the V_2O_5–CaO system.

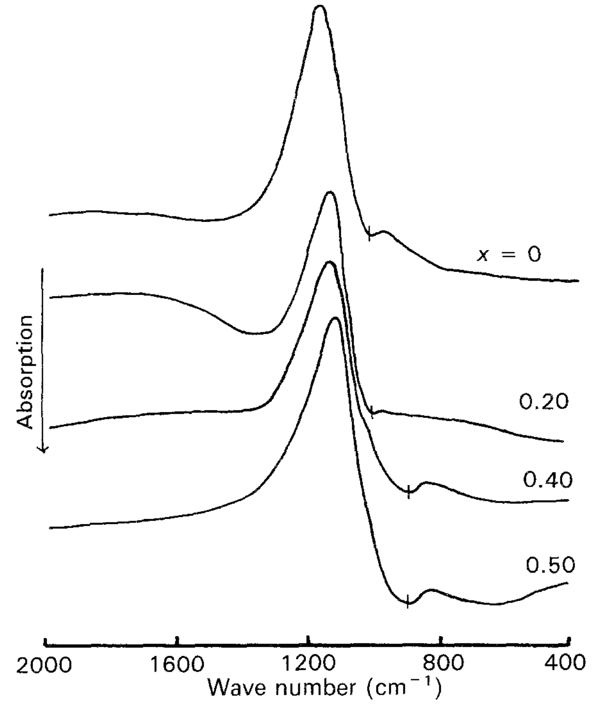

Figure 4 IR absorption spectra of the as-quenched glasses in the V_2O_5–BaO system.

3.3. Electrical conductivity of quenched glasses

The electrical conductivity of the glasses increased with temperature. The plots of log σ against $10^3/T$ are

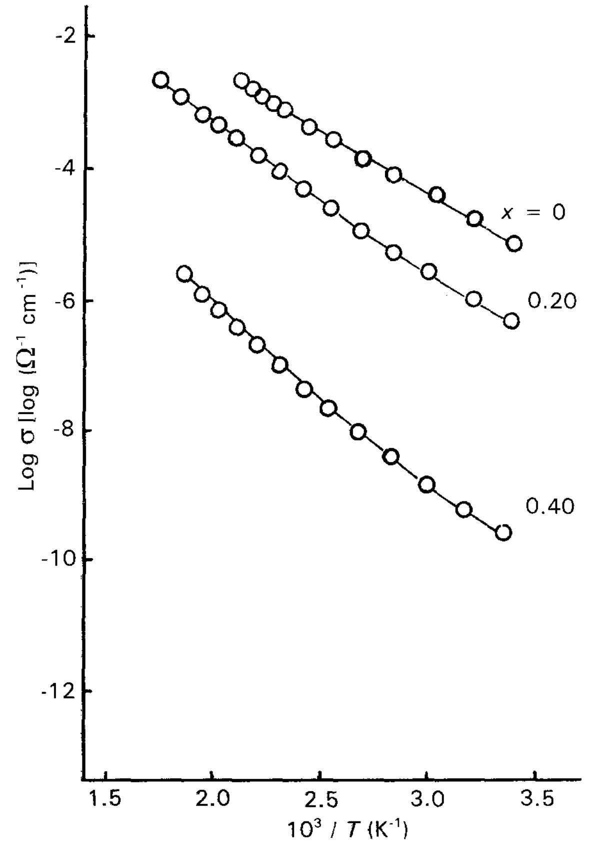

Figure 5 Electrical conductivities of the as-quenched glasses in the V_2O_5–MgO system.

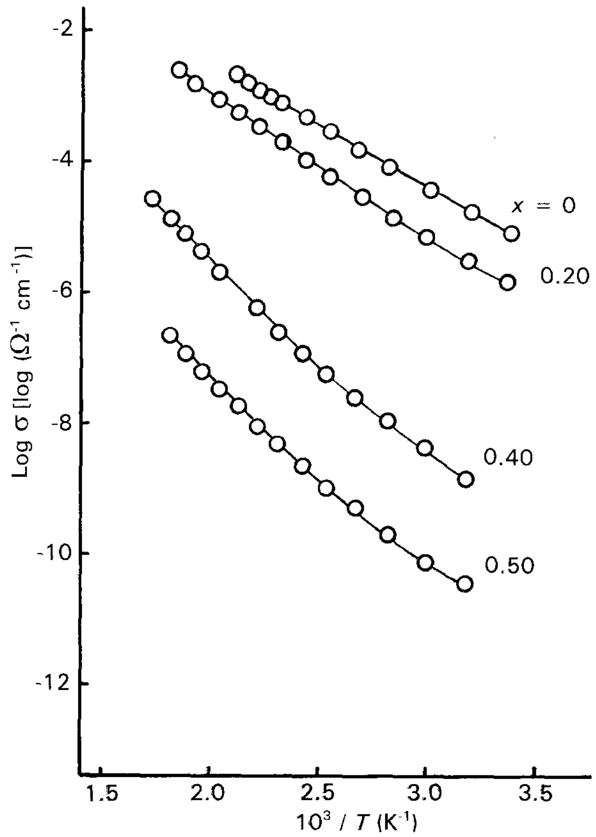

Figure 6 Electrical conductivities of the as-quenched glasses in the V_2O_5–CaO system.

shown in Figs 5–7. Deviations from the linear relation between log σ and $1/T$ towards the higher log σ side were observed for the low conductive glasses. These are attributed to adsorption of H_2O on the glass surface. In all three systems, the conductivity was lowered with increasing x. The activation energies were calculated from the slope of the linear region of the log σ against $10^3/T$ plots. The activation energy for the V_2O_5 glass was 0.40 eV and increased with increasing x. The activation energies for the glasses of $x = 0.20$ were nearly same (about 0.42 eV) in all three systems, but the activation energies for the glasses of $x = 0.40$ and 0.50 in the V_2O_5–BaO system (about 0.70 eV) were much higher than those (about 0.50 eV) for the glasses of the same x in the other two systems.

The electrical conduction in the vanadate glasses is electronic, based on the electron hopping between V^{5+} and V^{4+} ions through the V–O–V bond in the glass network. Both the concentration of V^{4+} ions and the number of the V–O–V hopping path influence the conductivity. In all three systems, M^{2+} ions act as glass modifiers and are located between the glass network. Although the amount of V^{4+} ions in the glasses is too small to detect by the TG measurements, some V^{4+} ions must exist in the glasses. From the colour change of the glasses, the concentration of V^{4+} ions decreases with increasing x. As shown by the IR spectral data, the glass structure changes from that based on the layered crystalline V_2O_5, to that based on the chain structure of metavanadate. The V–O–V bond used for the electron hopping decreases with increasing x, associated with the structural change of the glasses. Both the decreases in the concentration of V^{4+} ions and the number of continuous V–O–V bonds cause a large decrease in the conductivity.

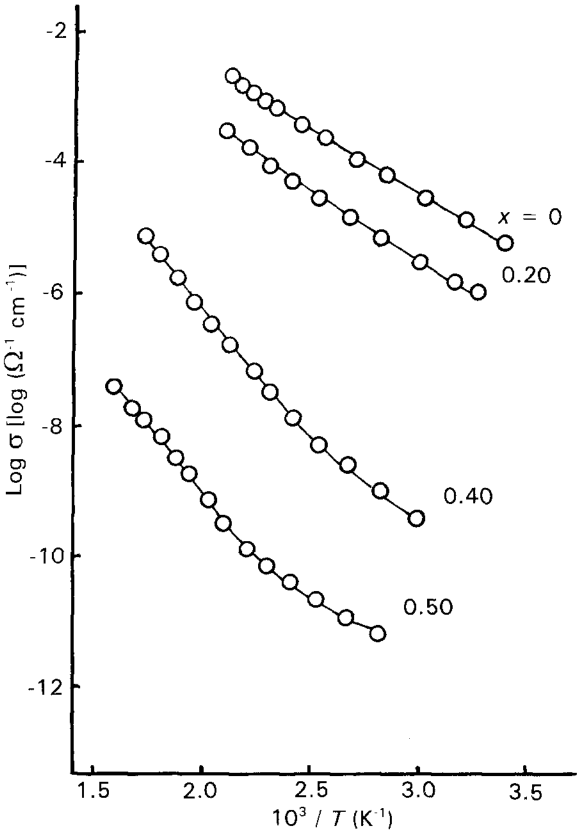

Figure 7 Electrical conductivities of the as-quenched glasses in the V_2O_5–BaO system.

4. Conclusion

Rapidly quenched glasses in the V_2O_5–MO (M = Mg, Ca and Ba) systems were prepared by a metallic twin roller. The glass-formation regions in the systems of M = Ca and Ba were a little wider than that of M = Mg. The crystallization temperature of the glasses rose with increasing MO content. No metastable phase was observed to form in the crystallization processes. The electrical conductivity of the glasses was lowered by an introduction of these glass-modifying ions. This behaviour could be explained on the basis of the glass structures estimated from the IR spectral data.

References

1. M. SAYER and A. MANSINGH, *Phys. Rev. B* **6** (1972) 4629.
2. B. V. JANAKIRAMA-RAO, *J. Am. Ceram. Soc.* **48** (1965) 311.
3. M. M. AHMED and C. A. HOGARTH, *J. Mater. Sci.* **18** (1983) 3305.
4. C. H. CHUNG and J. D. MACKENZIE, *J. Non-Cryst. Solids* **45** (1980) 357.
5. P. T. SARJENT and R. ROY, *J. Am. Ceram. Soc.* **50** (1967) 500.
6. Y. DIMITRIEV, I. IVANOVA and E. GATEV, *J. Non-Cryst. Solids* **45** (1981) 297.
7. Y. DIMITRIEV, V. DIMITROV, M. ARNAUDOV and D. TOPOLOV, *ibid.* **57** (1983) 147.
8. J. C. BOULOUX, J. GALY and P. HAGENMILLER, *Rev. Chim. Miner.* **57** (1974) 147.
9. M. TATSUMISAGO, T. MINAMI and M. TANAKA, *J. Am. Ceram. Soc.* **64** (1981) c-97.
10. M. MUNAKATA and S. IWAMOTO, *Bull. Electrotech. Lab.* **22** (1958) 816.
11. R. WOLLAST and A. TAZAIRT, *Silicates Ind.* **34** (1969) 42.
12. L. D. FREDERICKSON Jr. and D. M. HAUSEN, *Anal. Chem.* **35** (1963) 818.
13. H. G. BACHMANN, F. R. AHMED and W. H. BARNES, *Z. Krystallogr.* **115** (1961) 110.
14. H. N. NG and C. CALVO, *Can. J. Chem.* **50** (1972) 3619.
15. J. C. BOULOUX, G. PEREZ and J. GALY, *Bull. Soc. Fr. Mineral. Crystallogr.* **95** (1972) 130.

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