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Some physical studies on the xBeO(1 − x)V_2O_5 system

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The results of X-ray analysis, electron microscope studies, nuclear magnetic resonance, electron paramagnetic resonanace and infrared absorption spectra performed on the xBeO(1 − x)V_2O_5 system are reported. These suggest that, unlike previous statements, V_2O_5–BeO does not form solid solutions.

1. Introduction

It has been previously reported that solid solutions are formed in the V_2O_5–BeO system [1]. All the combinations prepared with V_2O_5 and BeO have about the same fusion temperature. This is attributed to the fluidity of the eutectic formed and the lack of intermediate compounds in the system.

In order to obtain information on the V_2O_5–BeO system, we prepared xBeO(100 − x)V_2O_5 binary samples, with $x \leqslant 10$ mol % BeO. These were investigated by X-ray, electron microscope, nuclear magnetic resonance, electron paramagnetic resonance and infrared absorption spectra. The conclusion from these studies is that V_2O_5 does not form solid solutions with BeO.

2. Sample preparation and structural studies

The samples were prepared from V_2O_5 and BeO having the purity 99.5 and 99.0%, respectively. The constitutents were dried, finely ground and kept in a desiccator with anhydrous calcium chloride. The constituents were mixed in suitable proportions, homogenized and then melted at 800° C for 1 h and relatively slowly cooled ($10^\circ\,C\,min^{-1}$) to a temperature somewhat lower than the melting point ($\sim 670^\circ$ C). After being kept at this temperature for 1 h, the samples were cooled slowly, together with furnace, and then ground. The colour of samples was dark brown, as previously stated [1].

The X-ray measurements were peformed with a Seifert-type apparatus, using Cu$K\alpha$ radiation ($\lambda = 0.15405$ nm). The diffraction patterns of the xBeO(1 − x)V_2O_5 samples show that the peaks are positioned at the same d_{hkl} values as in vanadium pentoxide. Thus, no evidence of composition dependence of the lattice parameters is observed. The differences between the X-ray patterns of V_2O_5 and those of the V_2O_5–BeO system consist only in the change of relative line intensities.

For electron microscope studies, the powdered samples were fixed in thin colodium films. The samples were investigated by using transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) methods with a TEMSCAM-200-CX electron microscope. In order to enhance the sample stability, under the action of electron beam irradiation, in the microscope, the grills were covered by vacuum evaporation with a 20 to 30 nm amorphous carbon film.

The V_2O_5–based samples were in the form of thin parallelepipeds with the (0 0 1)-type surface parallel to the film. The electron microscope image of the $97V_2O_5$–3BeO sample is presented in Fig. 1a. This consists of two superimposed V_2O_5 crystallites, slightly rotated, which determine the Moiré contrast. Evidence for dislocations is seen in the basal plane. The TEM patterns show only the presence of a V_2O_5–type structure (Fig. 1b).

The dislocation density increases as the BeO content increases. In Fig. 2a, the image of the $93V_2O_5$–7BeO crystal, in the (0 0 1) orientation is presented, and in Fig. 2c, the same zone inclined by 5° is shown. The contrast from Fig. 2c shows the presence of spheroidal formations, probably lenticular, oriented parallel to the (0 0 1) plane. Again the TEM patterns (Figs. 2b and d) show the presence of V_2O_5–type structure.

We carefully tried to find evidence, in V_2O_5–BeO samples, of the presence of phases other than the V_2O_5–type. No evidence of berylium oxide patterns or other compounds was observed. In some crystallites the 0.636, 0.378 and 0.319 nm reflections were shown. These seemed to be due to the presence of a VO_x structure induced by irradiation [2–4] even though the measurements were performed at small electron beam intensity ($1\,A\,cm^{-2}$).

3. Electron paramagnetic resonance and nuclear magnetic resonance studies

The electron paramagnetic resonance (EPR) studies were performed in the X-band (9.4 GHz), at room temperature by using JEOL-type equipment. The spectra consist of only one line, slightly asymmetrical, which is attributed to the presence of V^{4+} ions. No evidence of hyperfine splittings, characteristic of the interactions, between electronic and nuclear ($I = 7/2$) spins, respectively, are observed. Thus, the resonance

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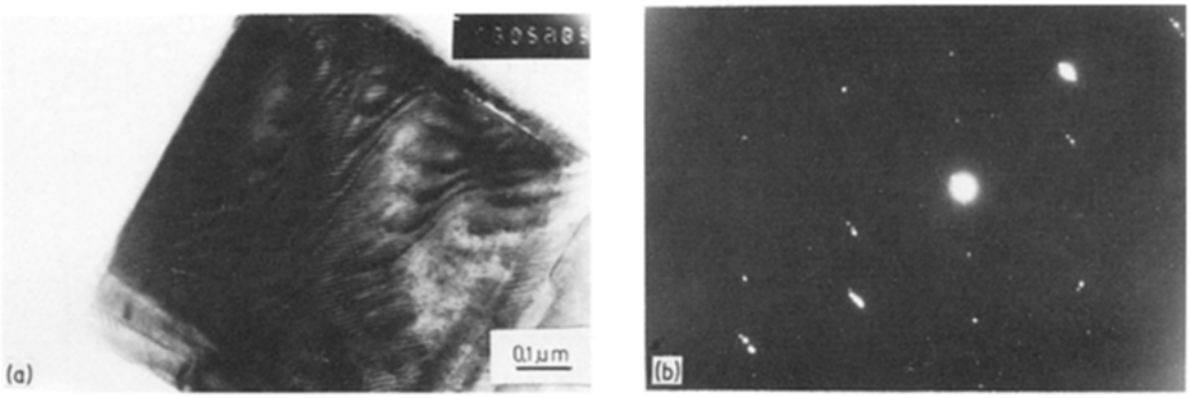

Figure 1 (a) The electron microscope image of the $97V_2O_5$–3BeO sample, and (b) the electron diffraction pattern.

spectra are due to the V^{4+} ions which interact as a result of their arrangement in clusters.

In Table I we give the linewidths, the resonance fields as well as the relative number of V^{4+} ions determined in xBeO$(1 - x)V_2O_5$ samples and also the data obtained for the $90V_2O_5$–$10MoO_3$ solid solution. The number of V^{4+} ions is not dependent on BeO content. The changes in the composition do not influence the resonance field values and the linewidths. This situation is different from that observed in interstitial (V_2O_5–Li_2O) or substitutional (V_2O_5–MoO_3) solid solutions, where the number of V^{4+} ions is strongly dependent on composition. This is due to the charge compensation of Li^+ and Mo^{6+} ions introduced into the lattice [5, 6]. As seen from Table I, the number of V^{4+} ions determined in the $90V_2O_5$–$10MoO_3$ solid solution is 40 times larger than that obtained in the $90V_2O_5$–10BeO sample.

The nuclear magnetic resonance (NMR) measurements were performed on ^{51}V, at room temperature, with JEOL-type equipment. Some NMR spectra are plotted in Fig. 3. In all cases, the presence of the central line, as well as four satellite lines equally spaced, is shown. By changing the BeO content, only minor modifications in the satellite line intensities are observed. These may be attributed to the lattice distortions (and/or deformations) [6].

In analysing the experimental data we consider a small quadrupole interaction, as compared to an electric field gradient, having axial symmetry [7]. In this case the NMR absorption frequencies $\nu_{m\to m-1}$ for polycrystalline samples are given by [4]

$$\nu_{m\to m-1} = \nu_0 + (2m - 1)\frac{1}{56}\frac{e^2qQ}{h} \qquad (1)$$

The quadrupole coupling constants (e^2qQh^{-1}), as determined from Equation 1 are plotted in Fig. 4. These are not dependent on composition and nearly

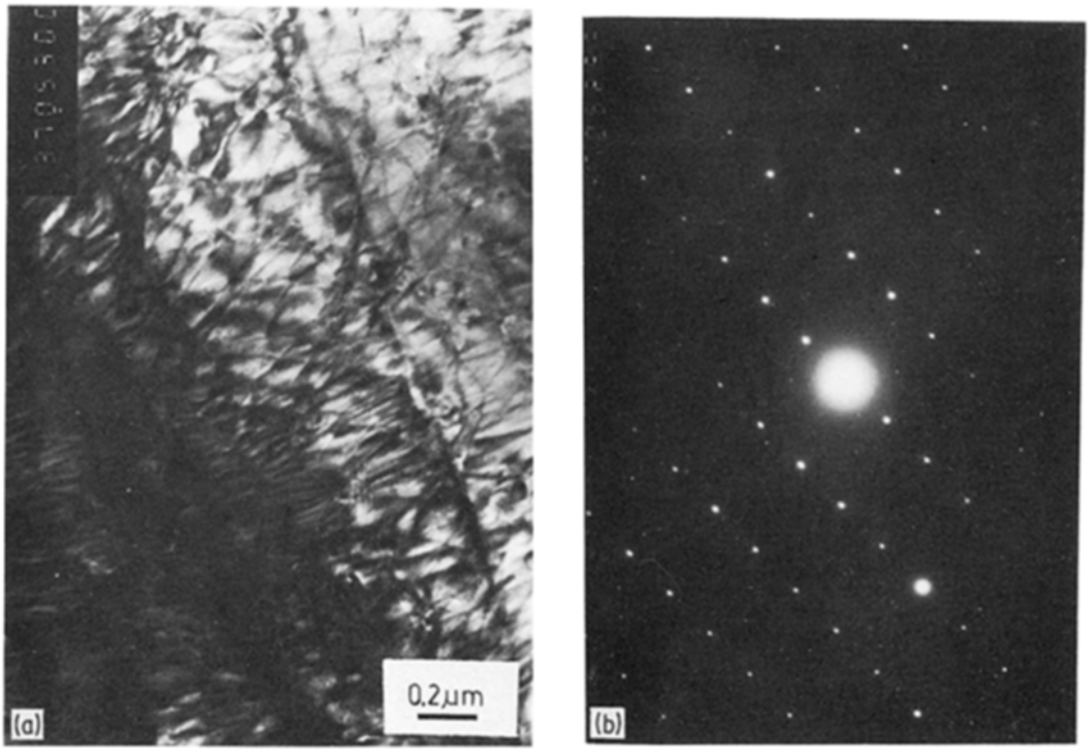

Figure 2 (a) The electron microscope image of the $93V_2O_5$–7BeO sample, and (b) the electron diffraction pattern. (c) The image of the same sample inclined by 5°, and (d) the corresponding electron diffraction pattern.

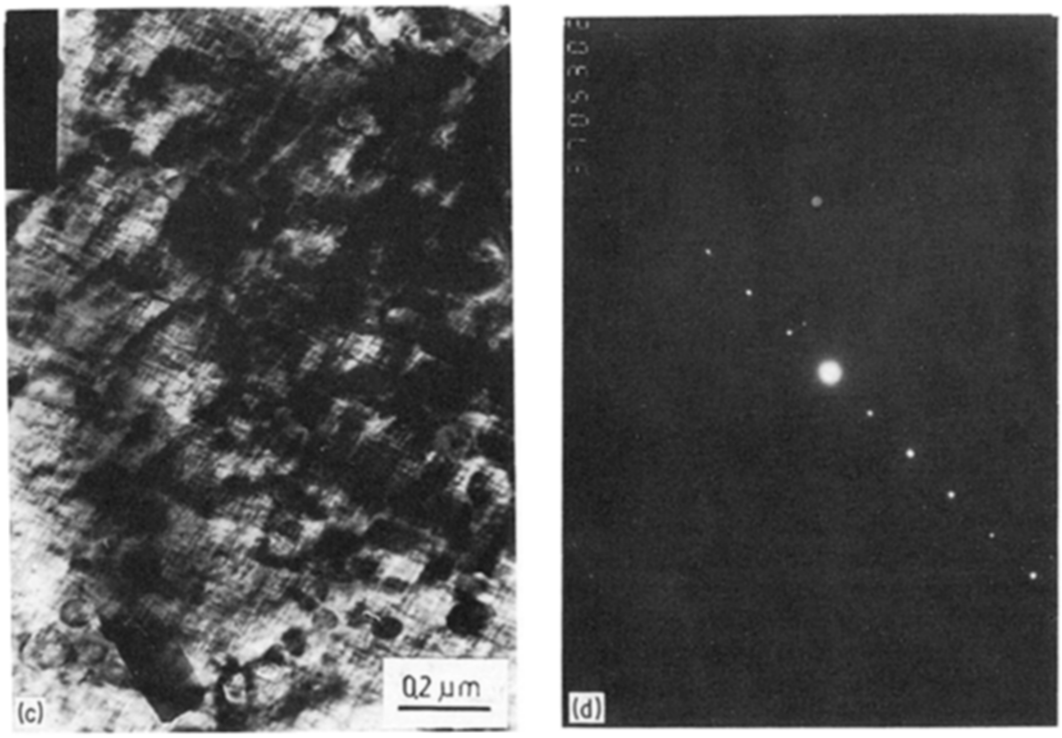

Figure 2 Continued.

the same as those determined in the V_2O_5 sample. This dependence is different from that seen both in substitutional and interstitial V_2O_5-based solid solutions [4, 6, 7].

4. Infrared absorption studies

The infrared absorption spectra were obtained by using an UR-20 spectrograph, at room temperature. Some spectra are plotted in Fig. 5. In the same figure, the spectrum of $95V_2O_5$–$5Li_2O$ solid solution is given.

The spectra of the V_2O–BeO system do not show modifications in the absorption bands, being nearly identical. Changes in the infrared spectrum are observed only in the $95V_2O_5$–$5Li_2O$ sample. The vibrations corresponding to V=O bonds take place along the *b*-axis of the V_2O_5 structure (Fig. 6) perpendicular to the (*ac*) plane, respectively. The V–O–V bonds are situated in the (*ac*) planes. The interstitial ions (for example Li^+) are also situated in the (*ac*) planes. The presence of these ions in the lattice leads to the modification of the $1020\,cm^{-1}$ band. This is reflected in the presence of some vibrations in the 950 to $990\,cm^{-1}$ bands, generated by the perturbative action of Li^+ ions on the vibrations of oxygen involved in vanadyl-type bonds. Similar spectra are seen in the V_2O_5–Fe_2O_3 system [8] where Fe^{3+} ions occupy both substitutional and interstitial sites in the lattice.

The fact that the $1020\,cm^{-1}$ band does not show modifications or deformations suggests that V_2O_5–BeO does not form interstitial solid solutions.

TABLE I The parameters of EPR spectra

Sample	Linewidth, $H_p \pm 10$(G)	Resonance field, $H_r \pm 5$(G)	The relative number of V^{4+} ions (±15%)
$97V_2O_5$–3BeO	540	3354	1.00
$95V_2O_5$–5BeO	520	3354	0.91
$93V_2O_5$–7BeO	530	3357	0.88
$90V_2O_5$–10BeO	580	3354	0.93
$90V_2O_5$–$10MoO_3$	800	3350	40

5. Discussion

The study of physical properties of the xBeO $(100 - x)V_2O_5$ system shows that the lattice constants are not modified by increasing BeO content. The electron microscope studies show evidence, in all cases, for the presence of a V_2O_5-type structure only. The number of V^{4+} ions, the quadrupole coupling

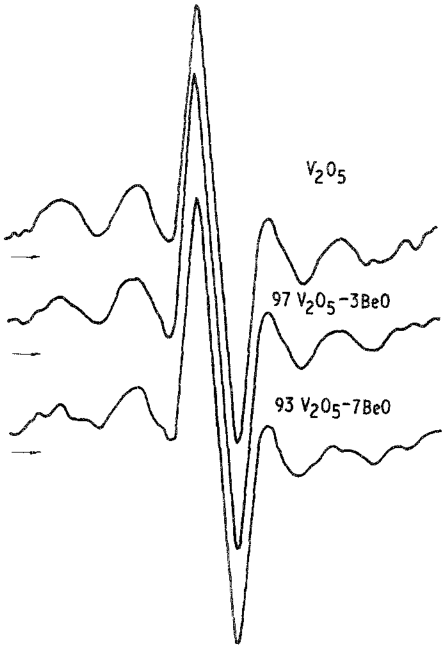

Figure 3 The ^{51}V NMR spectra in xBeO$(1 - x)V_2O_5$ samples with $x = 0$, 3 and 7 mol %, respectively.

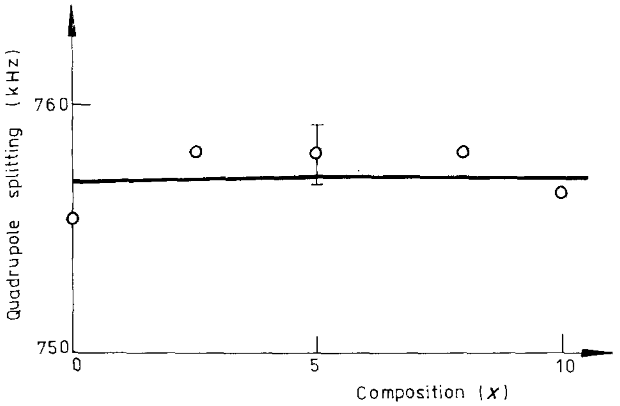

Figure 4 The composition dependence of the quadrupole coupling constants in xBeO(1 − x)V_2O_5 samples.

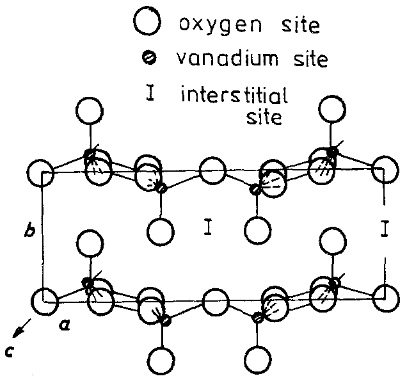

Figure 6 The crystalline structure of V_2O_5.

constants and the infrared spectra do not show composition dependence. This suggests that in the V_2O_5–BeO system, solid solutions are not formed.

By melting the constituents, an homogeneous liquid solution of BeO in V_2O_5 is formed. By cooling, at the solidification temperature, BeO is expelled from the V_2O_5 lattice, in the form of fine particles, having very small dimensions. Probably these particles agglomerate in lenticular formations, oriented parallel to the (0 0 1) plane. The BeO particles cannot be observed by X-ray and electron microscope studies, their dimensions being of the order of magnitude of the BeO lattice constants.

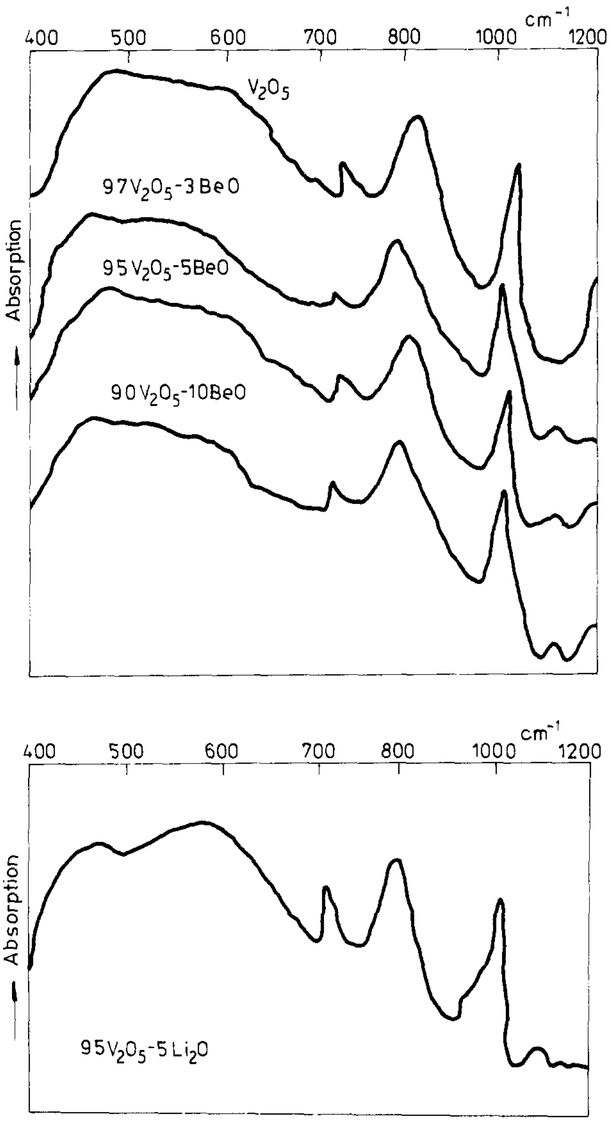

Figure 5 The infrared spectra for xBeO(1 − x)V_2O_5 samples with x = 0, 3, 5 and 10 mol % BeO as well as for $95V_2O_5$–$5Li_2O$ solid solution.

The expulsion of BeO particles is accompanied by the appearance of dislocations, or other imperfections of the V_2O_5 crystalline lattice. Their number increases when the initial BeO content increases. A similar behaviour was observed in the V_2O_5–Fe_2O_3 system [4]. The maximum number of Fe^{3+} ions introduced into the V_2O_5 lattice corresponds to 4 mol % Fe_2O_3, approximately equally distributed in interstitial and substitutional sites. A fraction of the initial Fe_2O_3 content has been expelled from lattice. Because of their small dimensions, the Fe_2O_3 particles cannot be observed by X-ray and electron microscope measurements. Their presence has been indicated only by Mössbauer effect studies [4].

Finally, we conclude that in the xBeO(100 − x)V_2O_5 system, solid solutions are not formed, for $x \leqslant 10$ mol % BeO.

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