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The Determination of the Crystalline Content of Glass-Ceramics

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The determination of the crystalline content of glass-ceramic materials is complicated by small crystal size (0.1 to 20 μm) as well as by variable crystal composition and morphology. Electron microscope, X-ray diffraction, and chemical separation techniques for quantitative crystallinity determinations can give equally valid results. Electron microscopy, however, is more universal in its application, since identification and synthesis or insolubility of the crystals are not important factors in quantitative results.

Replica and transmission electron microscopy are used to determine the crystalline content of complex polycrystalline glass-ceramics. These techniques involve preparation of replicas of selectively etched surfaces as well as thin sections less than 0.1 μm thick. The X-ray diffraction peak-intensity procedure for quantitative crystallinity analysis is demonstrated in glass-ceramics exhibiting extensive crystal solid solution. Chemical separation techniques for quantitatively distinguishing between glass and crystalline phases corroborate electron microscope and X-ray diffraction results.

1. Introduction

Glass-ceramics are polycrystalline materials produced by high-temperature controlled nucleation and crystallisation of glass [1-4]. The dynamic solid-state nucleation and crystal-growth processes required to bring about the transition of glass to polycrystalline materials often involve crystal phase transformations and solid solution; the resulting glass-ceramics are characterised by high crystalline content and small crystal size (0.1 to 20 μm) as well as variable morphology and composition of the crystals [5].

Conventional methods for the determination of the crystalline content, such as X-ray diffraction, microscopy, and chemical separation, require careful application or modification, based on an understanding of the character of glass-ceramics, before reliable results can be expected.

The X-ray diffraction, crystalline scattering, peak-intensity method, well summarised by Klug and Alexander [6], is applicable to glass-ceramic systems, although care must be exercised in identification of the crystalline phases present and in synthesis of crystalline standards. The X-ray, non-crystalline scattering technique, also discussed by Klug and Alexander [6], has been specifically applied to partly devitrified glass by Ohlberg and Strickler [7]. This X-ray method may be useful when the crystals in the glass-ceramic are difficult to resolve by electron microscopy techniques and when the characteristics of the amorphous phase are predictable.

Optical microscopy cannot as a rule resolve the small crystals found in many glass-ceramics. However, replica and transmission electron microscopy [8, 9] have been successfully applied in determining the percentage of crystallinity, and these techniques seem applicable to most situations.

The separation of the glassy phase from the crystalline phases in glass-ceramics, by differences in solubility in various chemical reagents, is an obvious technique for crystallinity analysis. Such a procedure has been reported by Schwiete

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[10] for refractory materials. Chemical separation cannot be universally employed, however, since solvents cannot always be found which sufficiently differentiate amorphous from crystalline phases to provide quantitative separations.

2. Experimental

An RCA EMU-3G electron microscope was employed to obtain replica and transmission micrographs. Replicas were prepared by slightly etching a polished surface of the glass-ceramic to bring the glass or crystalline phases in relief, followed by conventional, platinum/palladium, preshadowed carbon-replica techniques [8]. Crystal species relatively insoluble in etch solvents were extracted and attached to carbon films for electron diffraction examination by over-etching procedures [8]. Thin sections of glass-ceramics, some as thin as 500 Å, were made by modifying the procedure of Doherty and Leombruno [9].

The main steps in the thin-section preparation, illustrated in fig. 1, were: mechanically polish one surface of the specimen (a); vacuum deposit an aluminium film (b) to a light transmission of approximately 35% on the polished surface, and heat to 300° C to increase film adhesion; mount the film side of the specimen with polyvinyl acetate adhesive (PVAc) (c) to a polystyrene slug (d); grind and polish the opposite side of the specimen (e) until the edge is less than 1000 Å thick, the thickness being monitored by interference colours from the aluminium film observed with an optical microscope; cover the polished surface (e) with polyvinyl alcohol and 3% acetic acid (PVA-HAc) support (f); dissolve the polyvinyl acetate adhesive (c) and the polystyrene slug (d) in benzene; cut selected specimen areas to fit microscope specimen screens; place selected areas on specimen screen (g) with aluminium coated side (b) in contact with screen; dissolve polyvinyl alcohol support (f) and aluminium film (b) in 0.1% NaOH (3 to 5 min required); finally, vacuum deposit a carbon film about 100 Å thick on the thin section to provide a conductive surface.

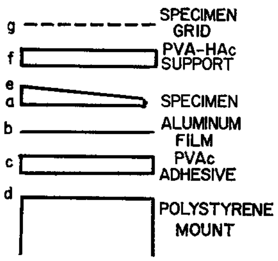

Figure 1 Thin-section preparation for transmission electron microscopy.

The vol % crystallinity was obtained from replica and transmission micrographs by the point-counting method described by Carrier [8]. Conversion of vol % to wt % crystallinity can be accomplished provided the density of the glass-ceramic and the crystalline phase or phases can be measured or are known from the literature.

X-ray diffraction examination was accomplished using CuKα radiation. Data were obtained with a Norelco X-ray generator and diffractometer used in conjunction with a Hamner detection system equipped with a pulse-height analyser. All materials examined were ground to pass a 400-mesh sieve, and all measurements were made on the ground specimens packed in a rotating sample holder. Crystalline materials used for standards were prepared by solid-state high-temperature reactions of finely ground and well-mixed ingredients in proper stoichiometric proportions. Repeated grinding, mixing, and firing were carried out in each preparation until optical microscope and X-ray examination indicated that the crystallisation reaction was complete and no glass was present. After identification of the crystalline phase in the glass-ceramic and the synthesis of a matching crystalline standard, the quantitative analysis of the crystalline content of the glass-ceramic was carried out by the internal standard/integrated diffraction peak-intensity method [6, 12].

Chemical separations of the vitreous and crystalline phases were made in polyethylene or Teflon containers. Usually rather small amounts of sample were treated by stirring with relatively large volumes of solution, such as 0.1 to 1.0 g of sample ground to pass 325 mesh, or finer, with 300 to 1000 ml solution. Extraction times varied from a matter of minutes to hours or days, depending on the system involved. Short-time leaching reactions with hydrofluoric acid were stopped by the addition of a slight excess of boric acid. Filtration was accomplished with the aid of vacuum, using membrane filters and stainless-steel funnels manufactured by the

Gelman Instrument Co*. Ignition of the separated crystalline phases, to remove the filter medium prior to weighing, was carried out in tarred platinum crucibles. The choice of suitable solvents, to separate quantitatively glass and crystalline phases, was aided by electron microscope observations of replicas, although known solubility data were the principal basis for selection. Optical and electron microscopy and X-ray diffraction examination of the extracted crystalline residues, as well as the nature of the extraction curves obtained, were employed as evidence for quantitative separations.

3. Results and Discussion

Fig. 2 is a replica electron micrograph of a lithia/alumina/titania/boric oxide/silica glass-ceramic containing β-spodumene/silica solid solution as the major crystalline phase plus a lesser amount of rutile crystals. The β-spodumene appears as polygons about 1 to 2 μm in size occupying most of the micrograph area, while a few oblong rutile crystals can be seen elevated above the β-spodumene. By slightly over-etching, very small rutile crystals, not plainly visible in this replica micrograph, can be brought into relief near the centre of the β-spodumene crystals. The vitreous phase appears as odd-shaped depressions in the micrograph. The microstructure of the two rutile phases is more clearly indicated in the extraction carbon-film micrograph pictured in fig. 3. In addition to the rutile crystals exhibiting two morphological forms, this micrograph shows the remnants of the total glass-ceramic microstructure of β-spodumene and glass phase.

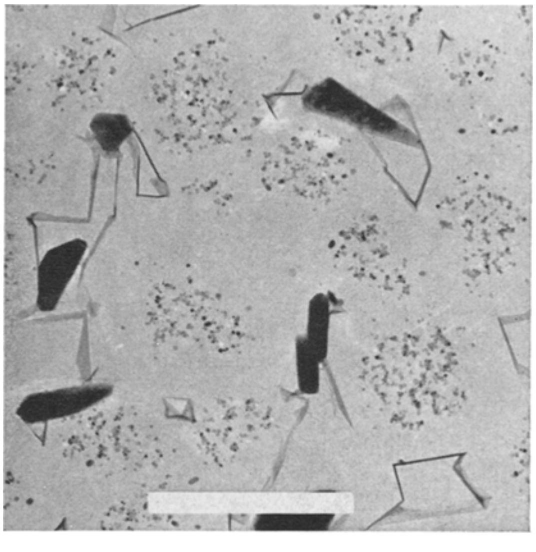

Figure 2 Replica electron micrograph of a glass-ceramic showing β-spodumene and rutile crystals in a glass matrix (white bar = 1 μm).

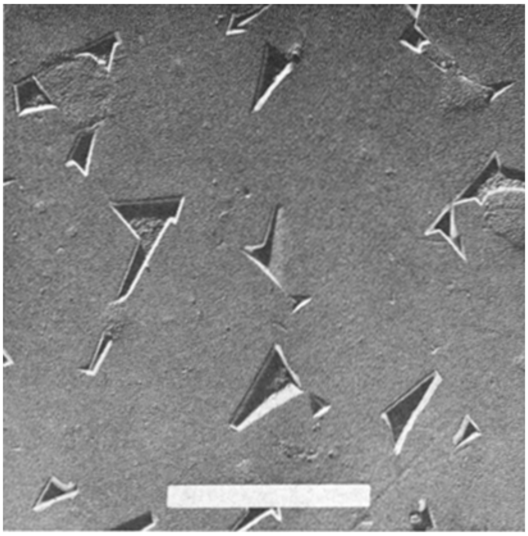

Figure 3 Extraction replica electron micrograph of a glass-ceramic showing two morphological forms of rutile crystals as well as outlines of β-spodumene and glass phases (white bar = 1 μm).

Figs. 4, 5, and 6 illustrate replica, transmission, and dark-field micrographs, respectively, of a baria/alumina/silica body containing mullite as the only crystalline phase. With the replica electron micrograph, areas can be recognised as crystalline owing to their polygonal shape. Frequently, extraction replicas and electron diffraction may also be used to confirm the crystalline nature of these same areas. In the dark-field electron micrograph, the bright areas represent crystals that are diffracting through the off-axis objective aperture, while the very dark areas represent crystals so oriented that electrons diffracted by them are intercepted by the objective aperture. The grey areas represent amorphous regions which have scattered some electrons through the objective aperture. The mullite crystals in this specimen were approximately 1000 × 1000 × 2500 Å in size. From visible light interference effects, the

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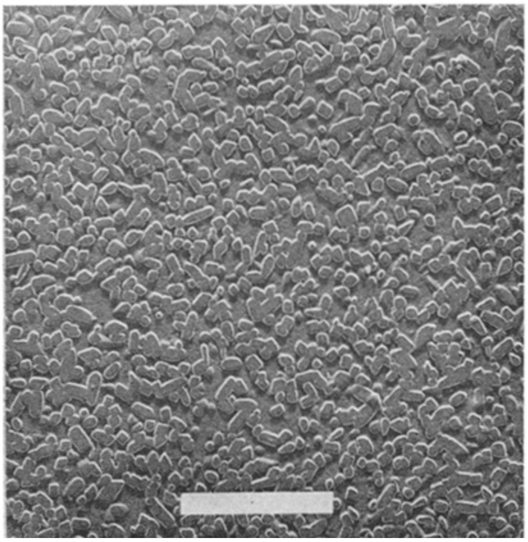

Figure 4 Replica electron micrograph of a partly crystallised glass showing mullite crystals in a glass matrix (white bar = 1 μm).

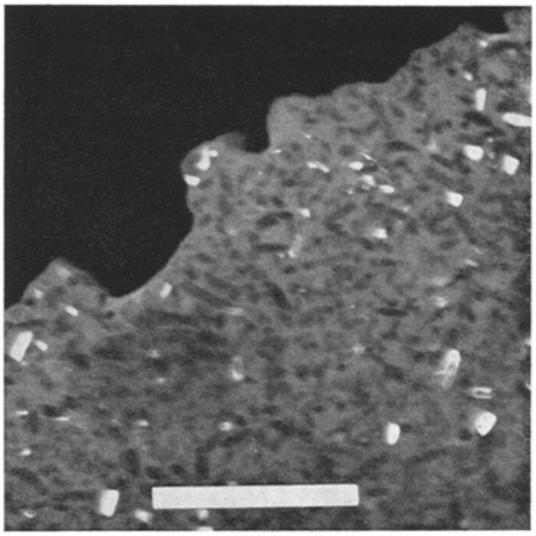

Figure 6 Dark-field transmission electron micrograph of the partly crystallised glass of fig. 4 (white bar = 1 μm).

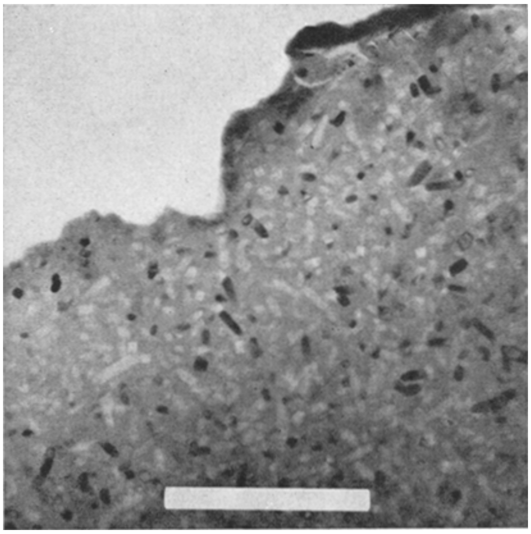

Figure 5 Bright-field transmission electron micrograph of the partly crystallised glass of fig. 4 (white bar = 1 μm).

thin section was determined to be less than 1000 Å thick.

The point-counting technique [8] was employed to obtain quantitative crystallinity analyses of a variety of glass-ceramic materials, the results of which are summarised in table V.

Quantitative X-ray diffraction crystallinity analyses were mainly confined to the major crystalline phase, β-spodumene/silica solid solution, observed in certain lithia/alumina/titania/silica glass-ceramic systems. The β-spodumene/silica solid solution in the lithia/alumina/silica system has been reported by Hatch [13] and by Roy *et al* [14]. Compositional information concerning the major crystalline phase was aided by comparison of *d* spacings and relative intensities of the diffraction peaks with the work of Skinner and Evans [11], who have described the crystal chemistry of β-spodumene/silica solid solution. Typical data for the interplanar spacing for the d_{303} diffraction peak for the solid-state-reaction crystalline materials and for several glass-ceramics, as well as extrapolated values taken from Skinner and Evans [11], are shown in table I. On the basis of *d* spacing data, the 1:1:7 lithia/alumina/silica/β-spodumene composition was selected as the best overall choice for a reference standard.

Three β-spodumene/silica solid-solution diffraction peaks, d_{201}, d_{102}, and d_{111}, were selected for analytical purposes. To assure that these diffraction peaks would give as consistent and valid information as possible, the measured integrated intensity ratios from the standards were compared with those of the glass-ceramic materials containing the unknown concentration of β-spodumene/silica solid solution. The integrated intensity ratios from the 1:1:7 and 1:1:8 solid-state crystalline reference materials,

TABLE I Comparison of d_{303} diffraction peaks.

Material	d_{303}, interplanar spacing (Å)	
	Observed	Skinner and Evans*
1:1:6 solid-state crystalline standard	1.930	1.930
1:1:7 solid-state crystalline standard	1.926	1.926
1:1:8 solid-state crystalline standard	1.922	1.922
Glass-ceramic 1	1.926	
Glass-ceramic 2	1.923	
Glass-ceramic 3	1.926	
Glass-ceramic 4	1.926	

*extrapolated data [11]

TABLE II Integrated β-spodumene/silica solid-solution diffraction peak-intensity ratios.

Material	Integrated peak-intensity ratios	
	d_{201}/d_{102}	d_{201}/d_{111}
1:1:7 solid-state crystalline standard	1.68	2.94
1:1:8 solid-state crystalline standard	1.66	2.92
Glass-ceramic 1	1.83	3.33
Glass-ceramic 2	1.75	3.08
Glass-ceramic 4	1.64	2.94
Glass-ceramic 4	1.66	2.93
Glass-ceramic 4	1.70	3.02

and three glass-ceramic materials on which quantitative analyses were made, are tabulated in table II. From the table, it can be seen that good agreement was obtained on all materials with the exception of glass-ceramic 1, where the ratios of both d_{201}/d_{102} and d_{201}/d_{111} differed by about 10% from the other materials. The variation in the integrated peak-intensity ratios given for glass-ceramic 4 represent the data obtained on three different samples and may reflect experimental error, or the result of minor changes in crystal character brought about by small differences in glass composition, melting, or heat-treatment.

Calibration standards were prepared using 1:1:7 lithia/alumina/silica air-quenched glass as the diluent, 20% excess NaCl as the internal standard, and the 1:1:7 β-spodumene/silica solid-state-reaction material as the crystalline reference material. Calibration curves were prepared employing calibration standards containing 25, 50, 75, and 100 wt % crystalline 1:1:7 reference material. The curves were obtained by plotting the integrated intensity ratios of each of the three β-spodumene diffraction peaks, d_{201}, d_{102}, and d_{111}, to the d_{220} diffraction peak of NaCl versus percentage of crystalline 1:1:7 β-spodumene. The d_{220} diffraction peak of the NaCl internal standard was selected for use because the d_{200} diffraction peak exhibited some variation in intensity in some sample preparations. Representative, measured, intensity ratios for the calibration standards and the ratios for three glass-ceramics are recorded in table III along with the β-spodumene/silica solid-solution concentrations found in the glass-ceramics analysed.

Reagents used for the chemical separation of a number of crystalline phases are tabulated in table IV, along with the phases exhibiting differential solubility and the time scale involved in the extraction. In each instance, the reagent completely dissolved the vitreous phase present. Typical plots illustrating rate of solution data in separating various crystalline components in glass-ceramics are presented in fig. 7. Also included are curves obtained for a borosilicate glass and for a material containing crystals in a predominantly glass matrix. Extrapolation of the linear portion of the curves to zero time

TABLE III Measured integrated diffraction peak-intensity ratios and β-spodumene concentrations.

Material	Diffraction peak ratios, spodumene/NaCl		
	d_{201}/d_{220}	d_{102}/d_{220}	d_{111}/d_{220}
25% crystalline standard	0.342	0.212	0.124
50% crystalline standard	0.666	0.430	0.249
75% crystalline standard	1.02	0.624	0.334
100% crystalline standard	1.36	0.815	0.464
Glass-ceramic 1	1.02	0.560	0.308
Glass-ceramic 2	1.20	0.695	0.394
Glass-ceramic 4	0.876	0.528	0.299
Glass-ceramic 4	0.838	0.493	0.278
1:1:8 solid-state material	1.36	0.832	0.466
	β-spodumene (wt %)		
Glass-ceramic 1	74.5	67.5	66.0
Glass-ceramic 2	89.0	83.5	84.5
Glass-ceramic 4	65.0	64.0	64.0
Glass-ceramic 4	62.5	59.5	59.5
1:1:8 solid-state material	101.0	100.0	100.0

TABLE IV Selected solvents for chemical separations.

	Reagent	Time scale	Phases exhibiting differential solubility
A†	H_2O	Hours	Soluble: high borosiliceous vitreous Insoluble: β-spodumene (SS)*, rutile, unidentified phases
B	0.5 N HNO_3	Hours	Soluble: high lead siliceous vitreous Insoluble: lead titanate (SS)
C	0.1 N HF (stopped by H_3BO_3)	Minutes	Soluble: alumino and borosiliceous vitreous Insoluble: β-spodumene, rutile, aluminium titanate
D	0.27 N HF	Hours	Soluble: siliceous vitreous, β-spodumene (SS) Insoluble: α-alumina, baddeleyite, mullite, rutile
E	0.27 N HF 0.30 N HCl	Hours	Soluble: baria siliceous vitreous Insoluble: mullite
F	1.25 N NaOH 0.9 N glycerine 0.001 N Na_2 EDTA	Hours	Soluble: siliceous vitreous, lithium metasilicate Insoluble: rutile, SnO_2, unidentified silicates

*solid solution
†These letters identify the reagents (see fig. 7).

was employed to estimate the insoluble crystalline component(s) present. It was found that care had to be exercised in extrapolation of the solubility plots. For valid results, clear indications of solubility differences had to be evidenced by rapid initial solution rates followed by much slower rates of solution.

The effect of the particle size of the sample being extracted is demonstrated in the two curves designated 3,C,M′ in fig. 7. The top curve illustrates data obtained on a sample ground to pass 325-mesh sieve, while the bottom curve was obtained on a reground portion of the same sample. While the slopes of the curves are different, both extrapolate to the same zero-time value.

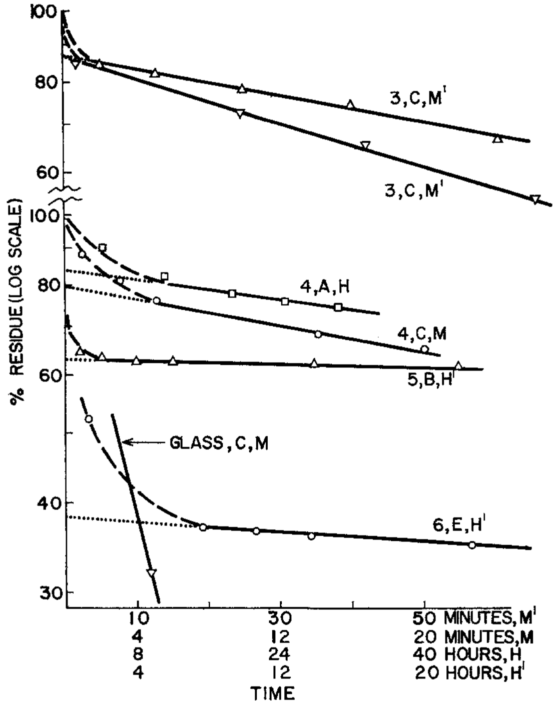

Figure 7 Typical rate of solution curves for several glass-ceramics in various reagents. Designations on the curves identify the materials as recorded in table V, extracted with the reagent recorded in table IV on the time scale indicated.

Coulter counter determinations of the particle size distribution of many of the ground samples as well as the extracted residues indicated that particle size distribution depended to some extent on the material. However, most of the samples examined contained particles in the range of 2 to 20 μm (spherical equivalent diameter) with 50 wt % or more of the sample less than 10 μm. Since the crystals of the major phase in the glass-ceramic materials being extracted averaged about 1 μm in size, some question concerning the effectiveness of the extraction was present, and examination of the extracted residues for vitreous phase was carried out by electron microscopy. Transmission electron micrographs of extracted particles did not indicate the presence of any amorphous phase. It was found that the particles were highly irregular in shape and that channelling of the extraction solvent into the interior of the particles had taken place to remove the vitreous phase. A typical micrograph of an extracted residue is illustrated in fig. 8.

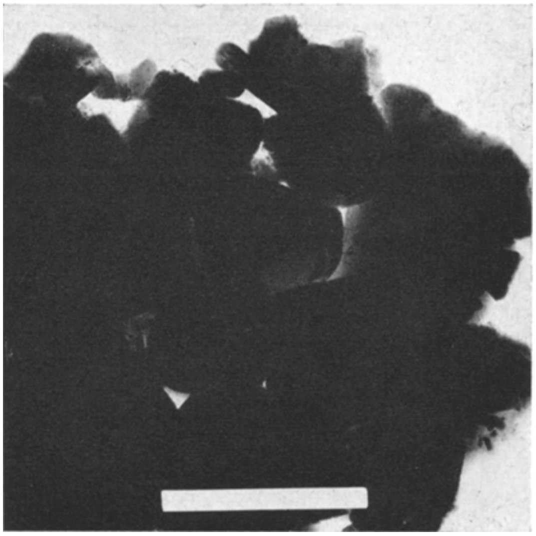

Figure 8 Electron micrograph of a ground particle of glass-ceramic which has been chemically extracted, showing removal of the glass matrix in the interior of the poly-crystalline particle (white bar = 1 μm).

The use of different extraction solvents to separate the crystalline phases in the same glass-ceramic is demonstrated by curves 4,A,H and 4,C,M in fig. 7. Plot 4,A,H represents the extraction of the sample with water on an hour time scale, while curve 4,C,M gives the data for the extraction with 0.1 N hydrofluoric acid on a minute time scale. In the latter case, the hydrofluoric acid leaching was stopped at specific times by the addition of a small excess boric acid to complex the reactive fluoride ion. Extrapolation of the two curves to zero time gave values of 83 and 80 wt % total crystalline content respectively.

A summary and comparison of quantitative analyses of a number of glass-ceramic systems by electron microscopy, X-ray diffraction, and chemical separation is recorded in table V. Electron microscopy values represent averages obtained from at least ten replica micrographs, while X-ray diffraction and chemical separation values are averages of at least duplicate determination in every case. Agreement between the three techniques for determining the crystalline content appears to be about ±10 % of the amount present in the examples illustrated. The good correlation with other experimental results and the relative simplicity and speed of the replica electron microscope method suggests that this

TABLE V Quantitative crystallinity analyses.

	Material	Crystalline content (%)^c		
	Composition field^a and crystalline phases determined^b	Electron microscope	X-ray diffraction	Chemical separation
1	Si/Al/Ti/Li			
	β-spodumene (SS) + $Al_2O_3 . TiO_2$	86		90
	β-spodumene (SS)	80	69	
2	Si/Al/Ti/Li/Mg			
	β-spodumene (SS) + rutile + cordierite	93		
	β-spodumene		86	
3	Si/Al/Ti/Li/B			
	β-spodumene (SS) + rutile	89		86
	β-spodumene	78	(82)^e	
4	Si/Al/B/Ti/Li/Mg			
	β-spodumene (SS) + rutile + unidentified	77		79
	β-spodumene	70	62	69
5	Si/Pb/Ti			
	Lead titanate (SS)	68		63
6	Si/Al/Ba^d			
	Mullite	39		38

The numbers in the first column identify the materials (see fig. 7).

(*a*) Elements excluding oxygen listed in decreasing concentrations present.

(*b*) Crystal phase identification by X-ray and electron diffraction as well as by morphology observed in replica electron micrographs.

(*c*) Electron microscope values in vol %, X-ray and chemical separation values in wt %.

(*d*) Material containing crystals in a predominantly glass matrix.

(*e*) Figure in parenthesis was obtained by Dr D. W. Lee, Arthur D. Little, Inc.

technique has the most universal application for quantitative crystallinity analyses of glass-ceramic systems.

Acknowledgements

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References

1. S. D. STOOKEY, *Glastech. Ber.*, V. Sonderband, Internationaler Glaskongress **32K** Heft 5 (1959) 1.
2. *Idem*, US Patent 2920971 (1960).
3. S. D. STOOKEY and R. D. MAURER, "Progress in Ceramic Science", Vol. 2 (Pergamon Press, Oxford, 1961).
4. S. D. STOOKEY, *Chem. Eng. News* **39** (1961) 116.
5. J. P. WILLIAMS and G. B. CARRIER, *Glass Technology* **4** (1963) 183.
6. H. P. KLUG and L. E. ALEXANDER, "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials" (Wiley, New York, 1954).
7. S. M. OHLBERG and D. W. STRICKLER, *J. Amer. Ceram. Soc.* **45** (1962) 170.
8. G. B. CARRIER, *ibid* **47** (1964) 365.
9. P. E. DOHERTY and R. R. LEOMBRUNO, *ibid*, p. 368.
10. H. E. SCHWIETE, *Glastech. Ber.* **34** (1961) 30.
11. B. J. SKINNER and H. T. EVANS, *Amer. J. Sci.* **258A** (1960) 312.
12. K. M. FINLAYSON and J. P. WILLIAMS, *J. Amer. Ceram. Soc.*, in press.
13. R. A. HATCH, *Amer. Mineralist* **28** (1943) 471.
14. R. ROY, D. M. ROY, and F. F. OSBORN, *J. Amer. Ceram. Soc.* **33** (1950) 152.