Vibration Eigenmodes and Size of Microcrystallites in Glass: Observation by Very-Low-Frequency Raman Scattering

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The observation of very-low-frequency bands by Raman scattering in a nucleated cordierite glass is described. The frequency of the maximum of scattering is proportional to the inverse diameter of the particles, which are spherical spinel microcrystallites. It is shown that vibrational surface modes of particles are responsible for this Raman scattering.

After the specific-heat measurements of small metal particles, carried out by Novotny, Meincke, and Watson,[1] and Novotny and Meincke,[2] many theoretical researches have been made on the lattice dynamics[3–7] of small particles. The vibrations of spherical particles have been studied a century ago by Lamb[8] who discussed the problem of the homogeneous elastic body in a spherical shape. Two types of modes, spheroidal and torsional, are derived from the stress-free boundary condition of a spherical surface. The recent theoretical works of Tamura and co-workers[6,7] are an extension of Lamb's theory and consider various effects surrounding a small particle: matrix effect, surface relaxation effect, local clamping effect, and shape effect.

The aim of the latest theoretical studies was principally to interpret the specific-heat measurements. However, it should be possible to observe by infrared absorption or Raman scattering the modes which obey the transition selection rules. Some years ago Hayashi and Kanamori[9] observed the Raman scattering from the surface phonon mode in GaP microcrystals. The energy of the observed modes was between the bulk TO and LO phonon peaks. In the work which is presented in this Letter we were rather interested in the Raman scattering from particle modes, the energies of which fall in the acoustic of the bulk, and which contribute to specific heat.

Actually, the first observation of particle modes by Raman scattering at very low frequency in a nucleated glass is presented in this Letter. This Raman spectroscopy follows a detailed study of nucleation and precise characterization of nuclei or microcrystals, carried out partially in our research group.[10,11]

The base glass, nucleation of which has been studied, has a composition close to that of the mineral cordierite: 52 SiO_2, 34.7 Al_2O_3, 12.5 MgO, with 0.8 Cr_2O_3 (wt.%). Nucleation was induced at a temperature higher than 800 °C by Cr^{3+} ions which are well known as a good nucleating agent. The characterization of nuclei or microcrystallites was carried out by several techniques. The size of the particles was determined principally by small-angle neutron scattering,[10] and also by small-angle x-ray scattering and electron microscopy.[12] The nature and structure of the microcrystallites were precisely determined by electron paramagnetic resonance,[10–13] laser spectroscopy,[11] and electron diffraction.[12]

The process of nucleation and crystallization was described as follows. At first there is a diffusion of Cr^{3+} ions in the glassy matrix giving rise to a clustering of these ions and the formation of a mixed $MgCr_2O_4$-$MgAl_2O_4$ spinel. Microcrystals appear and grow with the heating time. The samples studied by Raman scattering, the results of which are given in this Letter, contain microcyrstallites having a shape which in a first approximation can be considered as spherical. The diameters are between about 100 and 400 Å from neutron and x-ray scattering.

Raman scattering is a good technique to study the order at small or long distance in glasses. Shuker and Gammon were the first who showed by theory and experiment the breaking of the momentum selection rules by the disorder in amorphous materials and the possible observation of first-order Raman scattering by acoustic phonons.[14] Martin and Brenig gave a model which relates the maximum of Raman scattering, or the so-called "boson peak," with the correlation length in glass.[15]

Our experimental configuration to observe Raman scattering from the nucleated glass samples was conventional. The incident light was emitted by a 4-W argon laser. Various lines were used, in particular 4880 and 5145 Å with a mean power of 400 mW. Light scattered at $\pi/2$ from the incident beam was analyzed with a double monochromator, Jobin-Yvon model U1000. An EMI photomultiplier and a photon-counting system were used for detection.

In our cordierite samples a boson peak was observed at 80 cm^{-1}. After heat treatment, its intensity decreased and a new band at very low frequency appeared at the foot of the Rayleigh line.[16] Figure 1 shows the Raman scattering spectrum for a sample heat treated for 4 h at 875 °C and 2 h at 900 °C. In ad-
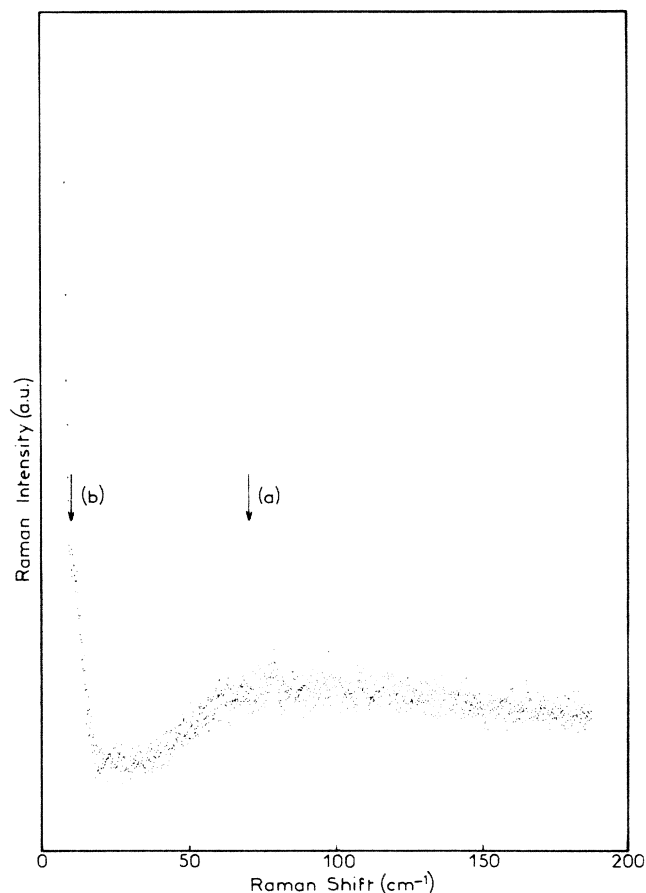
FIG. 1. Stokes Raman scattering for a cordierite glass sample heated 4 h at 875 °C and 2 h at 900 °C. Arrows indicate (a) the maximum of boson peak, (b) the band due to microcrystallites.
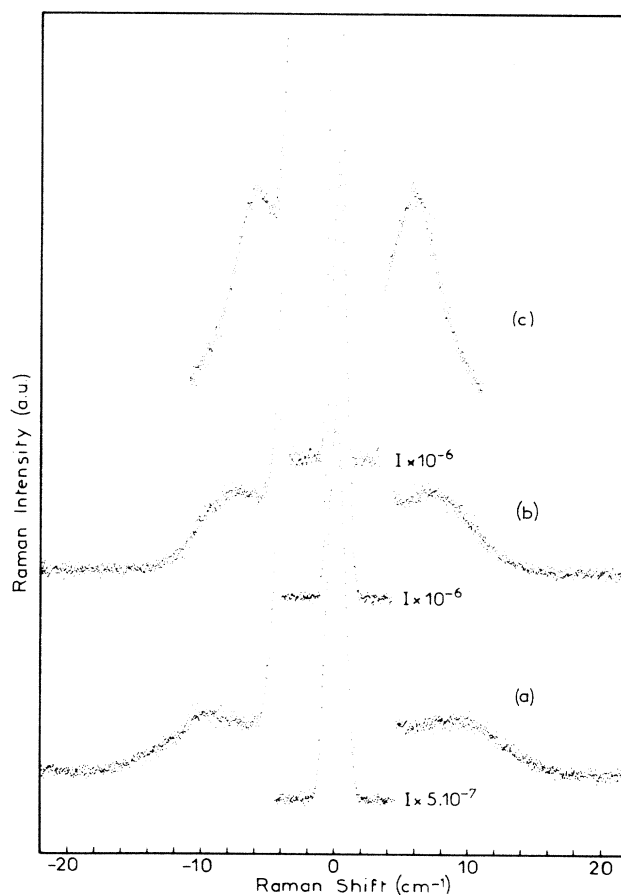

FIG. 2. Stokes and anti-Stokes very-low-frequency Raman-scattering bands due to microcrystallites after heat treatment. (a) 4 h at 875 °C and 2 h at 900 °C, (b) 4 h at 875 °C and 4 h at 900 °C, (c) 2 h at 875 °C and 10 min at 1050 °C.

dition to the boson peak, a band was clearly observed near the Rayleigh line (the maximum of the boson peak and the very-low-frequency band are indicated by arrows in Fig. 1).

These new Stokes and anti-Stokes bands which appeared with the nucleation are shown in more detail in Fig. 2 for different heat-treated samples or different sizes of particles. Several observations were made on these bands. The intensity increased with the size of the particles. By neutron scattering it was determined that the number of particles was constant after a pretreatment at 875 °C. The intensity of the bands decreased with the temperature and the variation was in agreement with a first-order Raman scattering. The new Raman bands are strongly polarized with the same polarization as the laser beam. This point is in agreement with the existence of spherical sources of scattering.[17]

The more interesting experimental result was the linear dependence of the position of the Raman peak on the inverse diameter of the particle or microcrystal-

lite as determined by small-angle neutron or x-ray scattering. The Raman shift is plotted against the inverse diameter in Fig. 3.

These different observations make it evident that the new Raman bands which appear with the nucleation of glass are due to scattering from spherical microcrystallites.

As mentioned before vibrations of a homogeneous elastic body of spherical shape have been studied by Lamb. Two types of modes are distinguished: spherical and torsional. The spheroidal modes are characterized by the angular momentum $l = 0, 1, 2, \ldots$, and by the numbers h or k such that

$$h = \omega a / v_l \text{ and } k = \omega a / v_t, \tag{1}$$

where ω is the pulsation, a the radius of sphere, and v_l and v_t the longitudinal and transverse sound velocity, respectively. The torsional modes are characterized by the angular momentum $l = 1, 2, 3, \ldots$, and the number k.

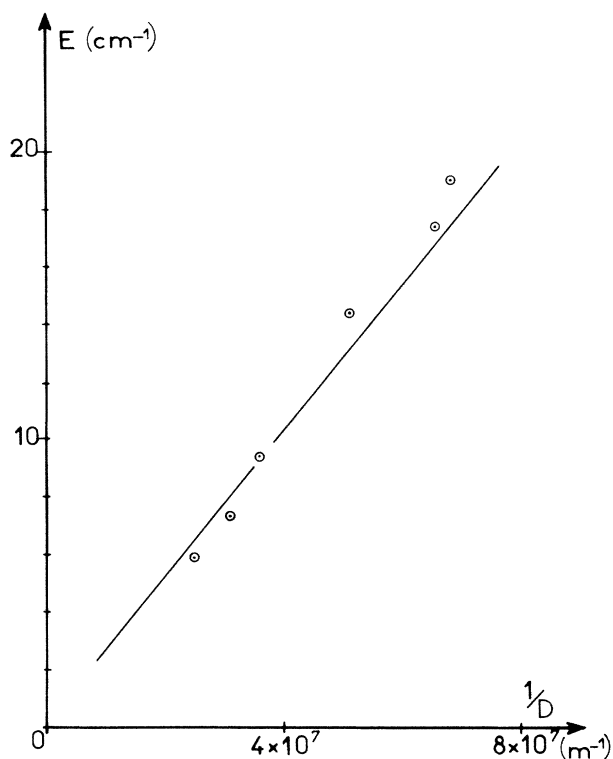The modes with smaller h or k have large amplitudes

FIG. 3. Position of the very low-frequency Raman peak as a function of the inverse of the particle diameter as obtained by small-angle neutron scattering.

at the particle surface and are considered as surface modes.[6] Tamura, Higeta, and Ichinokawa[6] have determined the matrix effect. A complete contact between particle and matrix eliminates the surface modes and softens the torsional modes. With partial contact or clamping the disappearance of surface modes is not evident. Furthermore, considering that the elastic properties of spinel microcrystallites are different from those of glass matrix (spinel is certainly much harder than the modified surrounding glass), one may think that surface or interface modes exist even with contact.

From selection rules only $l = 0$ and $l = 2$ modes can give Raman scattering of the light at first order. If one compares experimental results (Fig. 2) and the energy distribution of modes,[6] it appears clearly that only a narrow band of modes is responsible for the Raman scattering.

From Brillouin measurements the velocity of acoustic waves in a sample containing both an amorphous part and spinel microcrystallites is obtained[18] ($v_l = 7020 \pm 100$ m·s^{-1}, $v_t = 4025 \pm 50$ m·s^{-1}). From this, the velocity of sound in microcrystallites themselves can be estimated to be close to 8500 and 5500 m·s^{-1}, respectively. The frequencies of the different modes of a spherical particle are proportional to the inverse diameter: Experiment agrees with theory (Fig. 3). However, it appears that only modes with lower frequencies are active. From theoretical results of Lamb and Tamura et $al.$ the frequency ω_0^s (in cm^{-1}) of the lowest-energy spherical mode of a free particle of spinel corresponding to $l = 0$ is

$$\omega_0^s \cong 0.7 v_l / 2ac. \tag{2}$$

The frequencies ω_2^s and ω_2^T of the lowest-energy spheroidal and torsional modes, respectively, are practically equal:

$$\omega_2^s \cong \omega_2^T \cong 0.85 v_t / 2ac. \tag{3}$$

In these expressions c is the vacuum light velocity. The diameters $2a$ determined by Raman scattering are compared to the same diameter determined by elastic scattering (neutron, x ray, or electron) in Table I. Modes with higher frequency would give too large diameters.

Comparison between theory and experiment seems to indicate that only the lowest-energy modes or surface modes are active in Raman scattering from spherical particles. At the present time we have no sound explanation of this fact. But it is likely that there exists strong coupling between surface vibrational modes and surface electronic modes, the energies of which would be not very different from the incident photon energy.

TABLE I. Comparison of the particle's diameter as determined from small-angle neutron scattering and from Raman scattering [Eqs. (2) and (3)] for different heat treatment of the cordierite glass.

Heat treatment	Particle's diameter, elastic scattering (Å)	Particle's diameter obtained from ω_0 (Å)	Particle's diameter obtained from ω_2 (Å)
4 h 875 °C + 2 h 900 °C	220	212	166
4 h 875 °C + 4 h 900 °C	280	283	222
2 h 875 °C + 10 min 1050 °C	350	368	289

In Table I, it appears that the diameters given by Raman scattering from free particles are not very different from diameters obtained from elastic scattering (neutron, x ray, or electron). Therefore, from the above discussion it can be deduced that the contact between microcrystallites and the glass matrix is not very close.

The first observation of the eigenmode of a spherical particle by Raman scattering is interesting in itself. Furthermore, the experimental results described in this Letter show that the techniques of Raman scattering can be a simple and good method to determine the size of particles: aggregates or microcrystallites. Preliminary measurements have been carried out to study the nucleation in other glasses, oxides, or fluorides, where the nuclei are clearly observed by Raman scattering. This simple method is complementary to small-angle neutron or x-ray scattering. We can hope to observe particles the sizes of which vary between about 10 and 500 Å.

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