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OPTICAL PROPERTIES AND IONIC TRANSPORT DUE TO DEFECTS IN SiO_2

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Abstract: Defects and impurities in quartz and silica have been studied using different techniques. In quartz AC (10^2 - 10^5 Hz) conductance measurements have been performed on synthetic (Sawyer PQ) crystals extending the temperature range up to 1200°C and evidencing the β quartz-tridymite phase change. Optical absorption confirmed the existence, in silica, of two different variants of the B_2 absorption band (~ 5.1 eV), with correspondingly distinct luminescence spectra. The study of neutron irradiated SiO_2 did not confirm the proposed correlation between the B_2 and the E (7.6 eV) absorption bands.

1. Introduction

The presence of alkali ions (M^+), commonly acting as charge compensators at aluminium substitutional sites, is the origin of the charge transport that is observed in quartz after X or γ irradiation [1]. At temperatures above 100°C dissociation of the $\text{Al}-\text{M}^+$ occurs without the excitation by ionizing radiation. The dissociation energy and the migration energy of the freed M^+ ions have been calculated from AC and DC measurements [2]; in the present paper we report preliminary conductance results up to 1500 K, i.e. beyond the β quartz-tridymite phase change.

Radiation induced defects in amorphous and crystalline SiO_2 have been classified by optical absorption spectra since 1956 [3]. Some of them can be observed in as grown material as well. However the structure of most defects is still unknown. Recently new interest [4] rose about the luminescent B_2 band. In previous papers [5] it was pointed out that it is found only in oxygen deficient, in highly irradiated or in Ge doped silica. Two different defects have now been proposed to be associated to the B_2 band: one impurity-related and the other intrinsic.

In this paper we discuss the proposed models on the basis of our updated results.

2. Experimental

Crystalline samples, used both in the conductance and in the optical measurements, were disks few millimeter thick, cut from Sawyer PQ bars of synthetic quartz. The conductance measurements were done in a home made oven that can reach 1300°C in a 10^{-2} Pa vacuum, using a Gen Rad 1615A capacitance bridge. The obtained capacitance-resistance data have been analyzed by the complex impedance method [2].

Optical measurements were performed also on amorphous SiO_2 ; silica samples included all the four types in which glassy SiO_2 is classified [6]; type I (dry natural, i.e. Pursil K), type II (wet natural, i.e. Herasil), type III (wet synthetic, i.e. Tetrasil B) and type IV (dry synthetic, i.e. Tetrasil SE).

Some of the crystalline and pure silica samples have been exposed to nuclear reactor irradiation up to an integrated flux of 10^{19} neutrons/cm²; neutrons whose energy is in excess of 22.6 eV are 1/3 of the total flux. During irradiation the sample temperature was $65 \pm 2^\circ\text{C}$.

Optical absorption measurements were performed at room temperature using a Cary 2300 spectrophotometer and a vacuum ultraviolet apparatus; photoluminescence and its excitation were measured in a fairly sensitive apparatus described elsewhere [7]; all the spectra have been corrected for the optical response or efficiency of the apparatus.

3. Results and Discussion

i) Ionic conductance

We recently reported our results on quartz conductance measurements up to 1100 K [2]. We have then modified our apparatus that can now reach 1500 K. The results so obtained are reported in figure 1 in the form of $\ln(\sigma T)$ versus $1/T$. Comparing them with figure 2 of ref.2 we confirm the two slopes there observed, and can evidence a third slope (0.27 eV) at $T > 1100$ K.

This temperature is very close to the phase change in the SiO_2 structure, from β quartz to tridymite, that occurs at 1140 K. The obtained 0.27 eV value should then be the activation energy of the ionic conductance process in tridymite, just as the 0.67 eV value is in β quartz. Such a large difference is justified considering that the phase change induces a variation of density, from 2.65 to 2.30 gr/cm^3 , and a corresponding enlargement of the z-axis channels.

As regards the first to second slope variation (from 1.32 eV to 0.67 eV) a proposal was put forth [2], however new results in the radiation induced conductivity [8] together with a theoretical paper [9] on the potential of the $\text{Al}-\text{M}^+$ centers are the bases for reconsidering the interpretation model.

ii) Optical measurements

Prior to irradiation the B_2 absorption band (~ 5.1 eV) is present only in type I and type II silica. Confirming our previous observation [7] two slightly but significantly different absorption bands exist in this spectral region, as shown in figure 2a, 2b.

Also the luminescence spectra of all the above mentioned samples show either one of two distinct patterns:

(a) emission bands at 4.25 eV and 3.12 eV, whose excitation is at 5.10 eV ($\Delta E=0.5$ eV) and 5.12 eV ($\Delta E=0.46$ eV) respectively or
(b) emission bands at 5.45 eV, 3.12 eV and 2.7 eV excited at 4.96 eV ($\Delta E=0.4$ eV), 5.12 eV ($\Delta E=0.46$ eV) and 4.86 eV ($\Delta E=0.4$ eV). We report in figure 3a, 3b the excitation spectra of the high energy emission band for a typical sample of both groups.

The correlation between 5.14 eV, or 5.04 eV, B_2 absorption band and (a), or (b), luminescence is excellent; in confirmation of previous evidence [7,10,11] it can therefore be concluded that the nature of the so called B_2 absorption band and related photoluminescence is indeed composite (and not due to the OH content of the material, since no correlation has been found).

The 5.04 eV absorption band, but not the 5.14 eV, can be created in pure silica with neutron irradiation, giving rise to the 4.45 eV and the 2.7 eV photoluminescence; therefore these

bands must be ascribed to structural defects, while the 3.1 eV emission occurs at an impurity-related defect.

The composite nature of the B_2 band is therefore settled, at least experimentally. In ref.4 it has been proposed a model for the 5.04 eV B_2 band: the neutral oxygen vacancy ($\equiv Si-Si \equiv$); this hypothesis seems to us the most likely, in fact we have shown that no impurities are involved and the defect is intrinsic.

We found that neither of the B_2 variants is induced by particle irradiation in crystalline quartz; furthermore the study of absorption as a function of neutron dose in silica [11] does not confirm the correlation of the B_2 band with the E band (7.6 eV) reported in the literature [4,12]. Preliminary ESR results [13] indicate that in as grown samples the defect associated to the E band is not paramagnetic. We therefore suggest that, not being to be ascribed to the $\equiv Si-Si \equiv$ center, the E band can possibly be due to its Frankel pair counterpart: the peroxy linkage ($\equiv Si-O-O-Si \equiv$).

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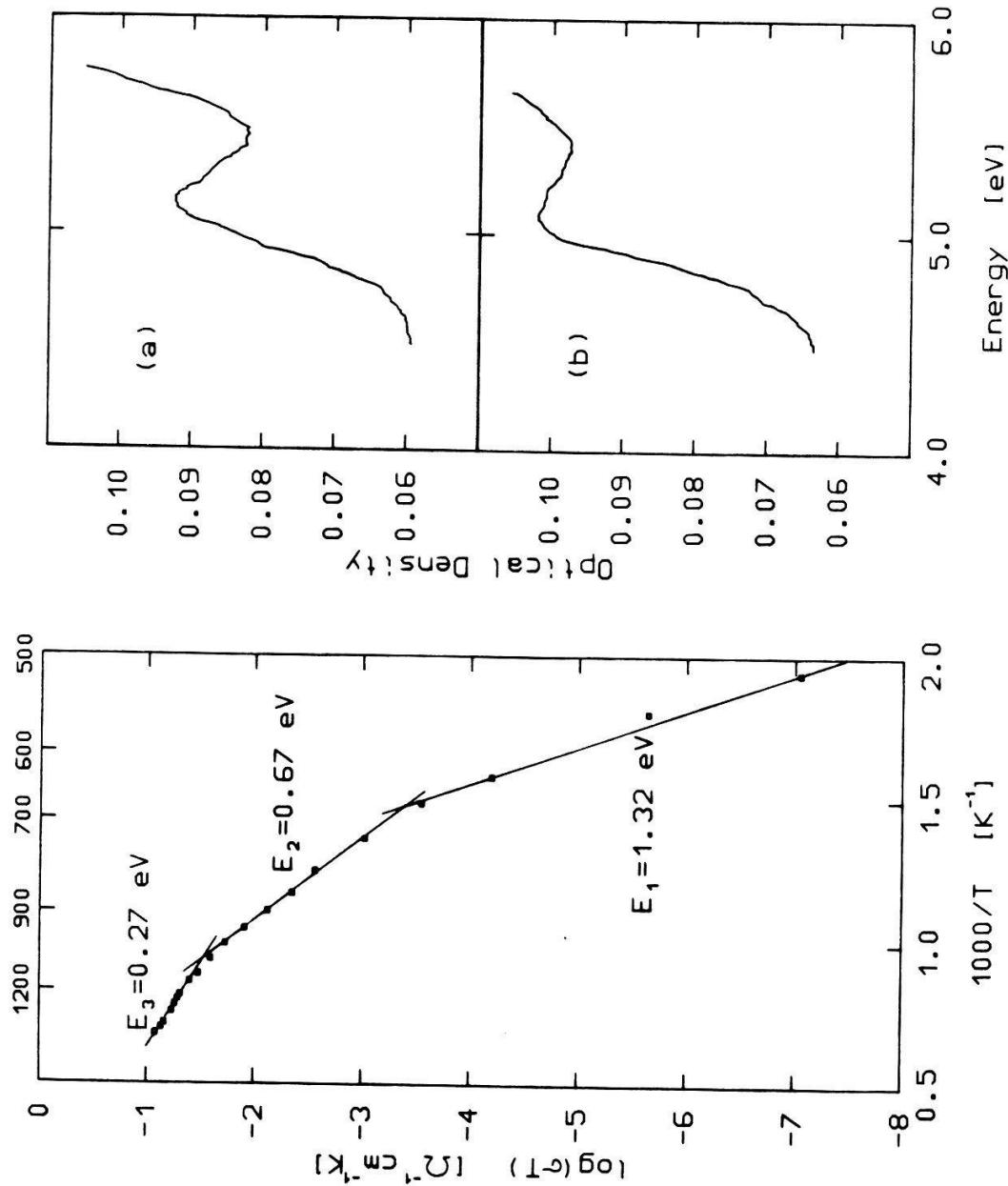


Figure 1: AC conductivity data for z-cut "as grown" Sawyer PQ quartz B₂ variants

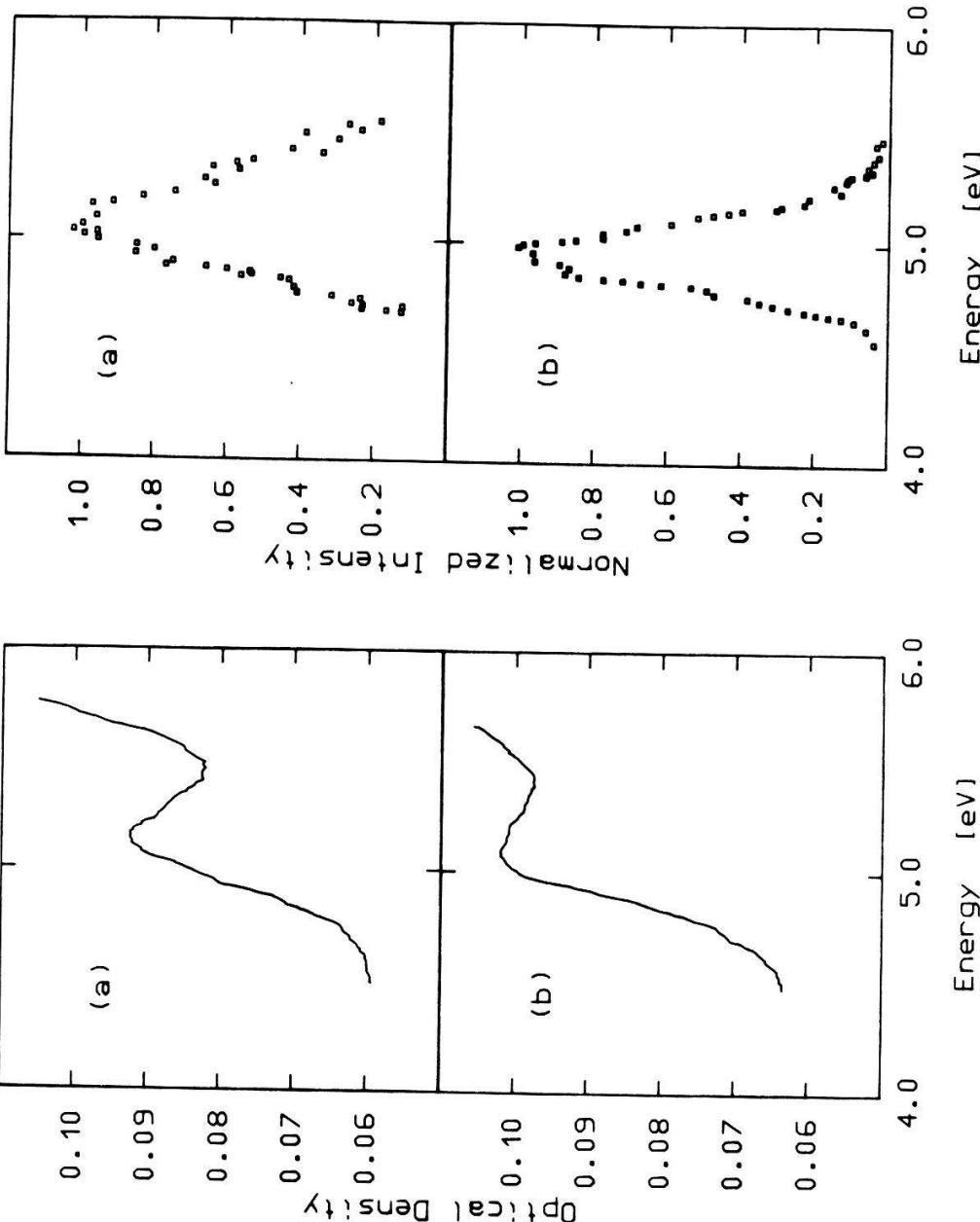


Figure 2: Absorption spectra of two type I silica samples showing the differences between the B₂ variants

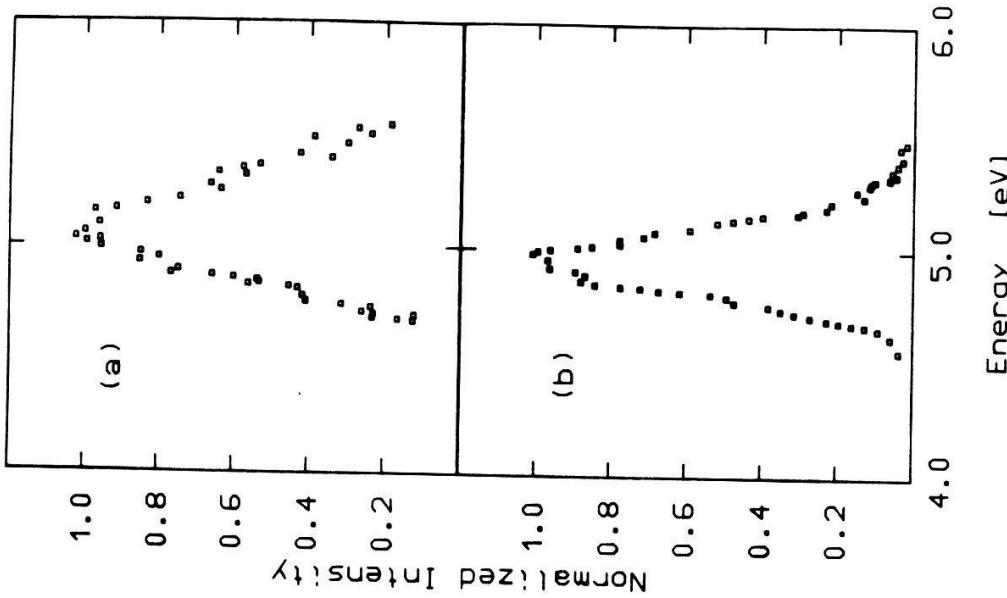


Figure 3: Photoluminescence excitation spectra of the high energy emission band (same samples as in figure 2)