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A new probe to change Curie temperature of $PbTiO_3$ sensors

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High temperature Raman spectra of nanocrystalline $Pb_{0.8}Ba_{0.2}TiO_3$, $Pb_{0.8}Sr_{0.2}TiO_3$, $Pb_{0.8}La_{0.2}TiO_3$ and $PbTi_{0.75}Zr_{0.25}TiO_3$, have been measured, as a function of particle size. There appears respectively a distinct temperature-induced soft mode phase transition in every sample whose Curie temperature can be determined from the mean-field theory. The detailed Curie temperature shift in modified $PbTiO_3$ ceramics by Ba, Sr, La and Zr, has also been investigated as a function of particle size, This study will favor preparations of high efficiency $PbTiO_3$ sensors with an adjustable Curie temperature.

I. INTRODUCTION

It is well known that pyroelectric infrared sensors show good sensing characteristics. Differing from photon sensors, they can be used at room temperature and their IR response does not depend on the wavelength of the IR radiation used. By combining these promising pyroelectric effects with sophisticated silicon IC technology, a realization of silicon monolithic IR sensor at near ambient temperature could be expected for a wide variety of applications. Nowadays, various kinds of pyroelectric materials like $LiTaO_3$ or TGS single crystals are commercially available. Among these materials, $PbTiO_3$ is a good candidate for IR detector because it has a large spontaneous polarization $P_s(75\mu C/cm^2)$ and a small dielectric constant (~ 100) along the polarization axis [1]. $PbTiO_3$ is a perovskite type of ferroelectric isomorphous with $BaTiO_3$ and its tetragonality(c/a=1 .06) is also very large [2]. But the Curie temperature T_c of $PbTiO_3$ single crystal is quite high, around 490 °C. For better sensitivity of detectors, the Curie temperature must be close to the operating temperature, In this sense, if the Curie temperature of $PbTiO_3$ could be reduced to about 160 °C by ionic substitution, its pyroelectric efficiency at room temperature can be strongly influenced. Obvious] y, the decrease of the Curie temperature T_c of $PbTiO_3$ can be realized by the substitution of of Pb or Ti ions. However, the substituted composition must have a suitable quantity in order to have appropriate T_c with high property coefficients. The experimental results show that the part substitution of Ba for Pb will lead to a decrease in Q and $\varepsilon_{33}/\varepsilon_0$, but an increase in k_p and a good frequency-temperature property. Practically, for materials used as ceramic wave filters and sonar emission vibration pickup, a high Q will be needed, But, in general, the material with a high Q has a low k_p. In materials with high ε there appears a large $\tan\delta$ and the materials with high k_p will probably lead to an unstable physical property. This reveals that it is very difficult to get an idea sensor with an appropriate T_c and high property coefficients only by dopants. Thus, it is essential to probe other ways to resolve this contradiction. So far, effects of particle size on physical properties and the Curie temperature T_c of materials have been widely received an increasing interest and attention[3-9]. For example, investigations for $PbTiO_3$ show that its Curie temperature can be lowered to room temperature as particle size is decreased to 12.6-20 nm. In this paper, we have made a detailed study for the modified $PbTiO_3$ by Ba, Sr, La and Zr as a function of particle size using Raman scattering spectroscopy.

II. EXPERIMENTAL

Nanocrystalline $Pb_{0.8}Ba_{0.2}TiO_3$(PBT20), $Pb_{0.8}Sr_{0.2}TiO_3$,(PST20), $Pb_{0.8}La_{0.2}TiO_3$ (PLT20) and $PbTi_{0.75}Zr_{0.25}TiO_3$(PZT25) with different particle sizes were separately prepared, using a sol-

gel process in which barium acetate, lanthanum acetate, strontium acetate, lead acetate, zirconium and titanium butoxide were used as the precursor materials. The processes involved dissolving the metal-containing compounds in the solvent, hydrolyzing and polycondensing the resulting solution into various gels, and finally heat treating these gels at different temperatures and for different time intervals to form nanocrystalline powders. Chemical phase analysis was done using powder XRD measurements. The average grain size was calculated from the full width at half maximum(FWHM) of the (111) diffraction peak using the Scherrer equation $d_{XRD}=K\lambda/\beta(\theta)\cos\theta$ [10]. Where λ is the x-ray wavelength, $\beta(\theta)$ is the FWHM of the diffraction line, θ is the angle of diffraction, and the constant $K\approx 1$. Raman spectra of the samples were measured using a Spex-1403 Raman spectrometer with a double monochromator, a standard photon-counting technique and an Ar^+ ion laser [1].

III. RESULTS AND DISCUSIONS

Raman spectra of PBT20, PST20, PLT20 and PZT25 with particle sizes of 60 nm, 37 nm, 54 nm and 44 nm are respectively shown in Fig. 1a - d. These spectra reveal the tetragonal structure of nanocrystalline materials at room temperature, similar to one observed for bulk $PbTiO_3$(PT) [12]. In earlier work, Ishikawa et al. had investigated samples with different average sizes as a function of temperature [13]. The T_c was indirectly measured as the temperature at which the frequency (ω_s) of the soft E(TO) mode ($\omega_s \rightarrow 0$ as $T \rightarrow T_c$) vanished. T_c was found to decrease with decreasing particle size with d_{crit}= 12.6 nm. On the other hand, in the case of bulk materials, the first phase transformation in $PbZr_xTi_{1-x}O_3$ (PZT) system was found to occur at x=0.52 [14-15], whereas no phase transformation was observed in bulk $Pb_{1-x}Sr_xTiO_3$ (PST) and $Pb_{1-x}Ba_xTiO_3$ (PBT) systems as x is increased from 0.0 to 1.0 [16-17]. Recent investigations on nanocrystalline PST, PBT, PZT and PLT with particle sizes of 37nm, 60 nm, 44 nm and 54 nm have shown that a phase transformation occurs at x=0.7, 0.7, 0.4 and 0.4 respectively [18-20]. According to these facts mentioned above, the samples used in present experiment are confirmed to have a tetragonal ferroelectric structure at ambient temperature.

From Fig. 1, it is found that the low frequency phonon mode of every sample, the E(TO) soft mode, shows a decrease in frequency, i.e. "softening", and widening in linewidth, on increasing temperature, as observed in pure bulk $PbTiO_3$. The dependence of the squared frequency of the soft mode upon temperature for PBT20, PST20, PLT20 and PZT25 is respectively displayed in Fig. 2a - d, revealing a nearly linear temperature dependence, in accordance with the soft mode theory in the mean-field approximation [21].

It should be noted that, because of a strong stray light in these materials, especially in PBT20, it is very difficult to measure the lowest frequency of the soft mode close to T_c. This is merely done by extrapolation of the observed data. The Curie temperature of pure $PbTiO_3$ is found to decrease on decreasing the particle size. Thus, it is reasonably considered that PBT20, PST20, PLT20 and PZT25 also undergo a similar temperature-induced soft mode as in pure $PbTiO_3$.

A detailed particle size dependence of the Curie temperature in the above mentioned materials has been performed and illustrated in Fig. 3a-d. One may notice that the transition temperature from cubic (CP) to tetragonal (TP) is shifted towards a lower temperature with decreasing particle size in nanocrystallines.

A careful observation reveals that the particle size corresponding to a Curie temperature of 20 ^oC in PBT20 and PST20 is smaller than that in PLT20 and PZT25. The particle size dependence of Curie temperature in PZT25 is also found to have a slow change above the particle size of 40 nm, which differs from that in PBT20, PST20 and PLT20. This may originate from many factors, for example, different chemical properties of Ba, Sr, La and Zr as well as their different ion radii(Ba^{2+} -0.143 nm, Sr^{2+} -0.127 nm, La^{3+} ~ 0.122 nm, Zr^{4+} -0.079 nm) will lead to various distortions of TiO_6 octahedra thereby changing the short-range forces responsible for the phase transitions. In addition, the particle size dependence of T_c may result from different substitution forms of Ba, Sr and La ions for Pb ions at A sites, and Zr for Ti ions at B sites in ABO_3 perovskite oxides.

The softening and widening of the soft mode caused by decreasing particle size, as observed by increasing pressure, have been measured in many nanocrystalline materials including $PbTiO_3$.13 As particle size of materials is decreased, the surface stress on particles will produce an additional effect on atoms inside particles due to some interfaces and spherical particle distribution. The additional effect is similar to that of hydrostatic pressure on atoms. Hence, the decrease of the Curie temperature with reducing particle size results from effects of surface stress of spherical particles.

IV. CONCLUSIONS

High temperature Raman spectra for PBT20, PST20, PLT20 and PZT25 with various particle sizes have been measured and their Curie temperature can be determined by the temperature dependence of the squared frequency of the soft mode which is consistent with the mean field approximation. The Curie temperature is found to shift towards a lower temperature with decreasing particle size and it depends upon the substitution forms of doping ions for the ions at A and B sites in ABO_3 perovskite materials. The surface stress from small particles plays an important role in lowering Curie temperatures relative to the corresponding bulk materials. Our study will offer a physical basis for preparing $PbTiO_3$ sensors with an adjustable Curie temperature.

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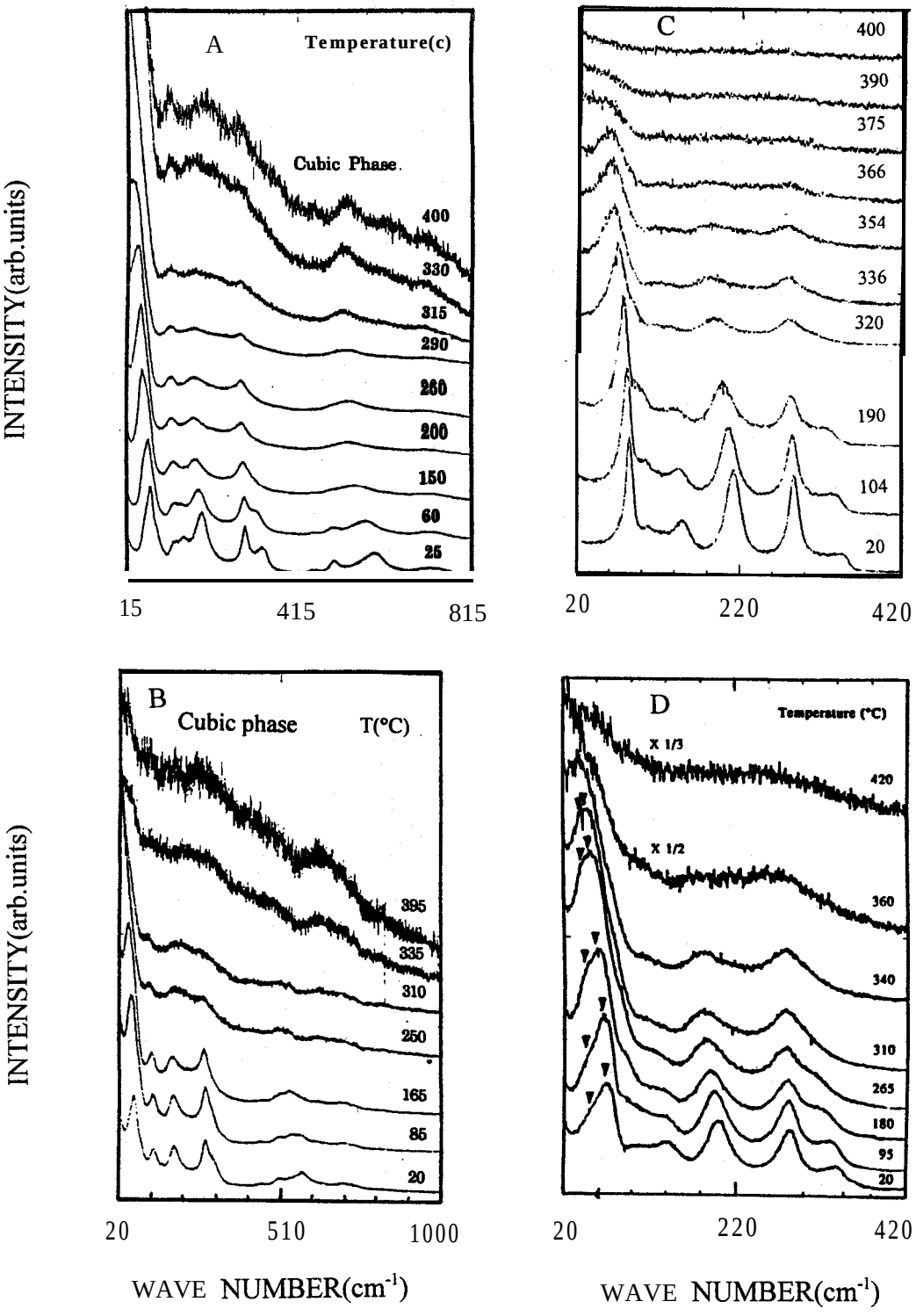

Fig. 1 Raman spectra of nanocrystalline materials at various temperatures

A. $Pb_{0.8}Ba_{0.2}TiO_3$ B. $Pb_{0.8}Sr_{0.2}TiO_3$

C. $Pb_{0.8}La_{0.2}TiO_3$ D. $PbTi_{0.75}Zr_{0.25}O_3$

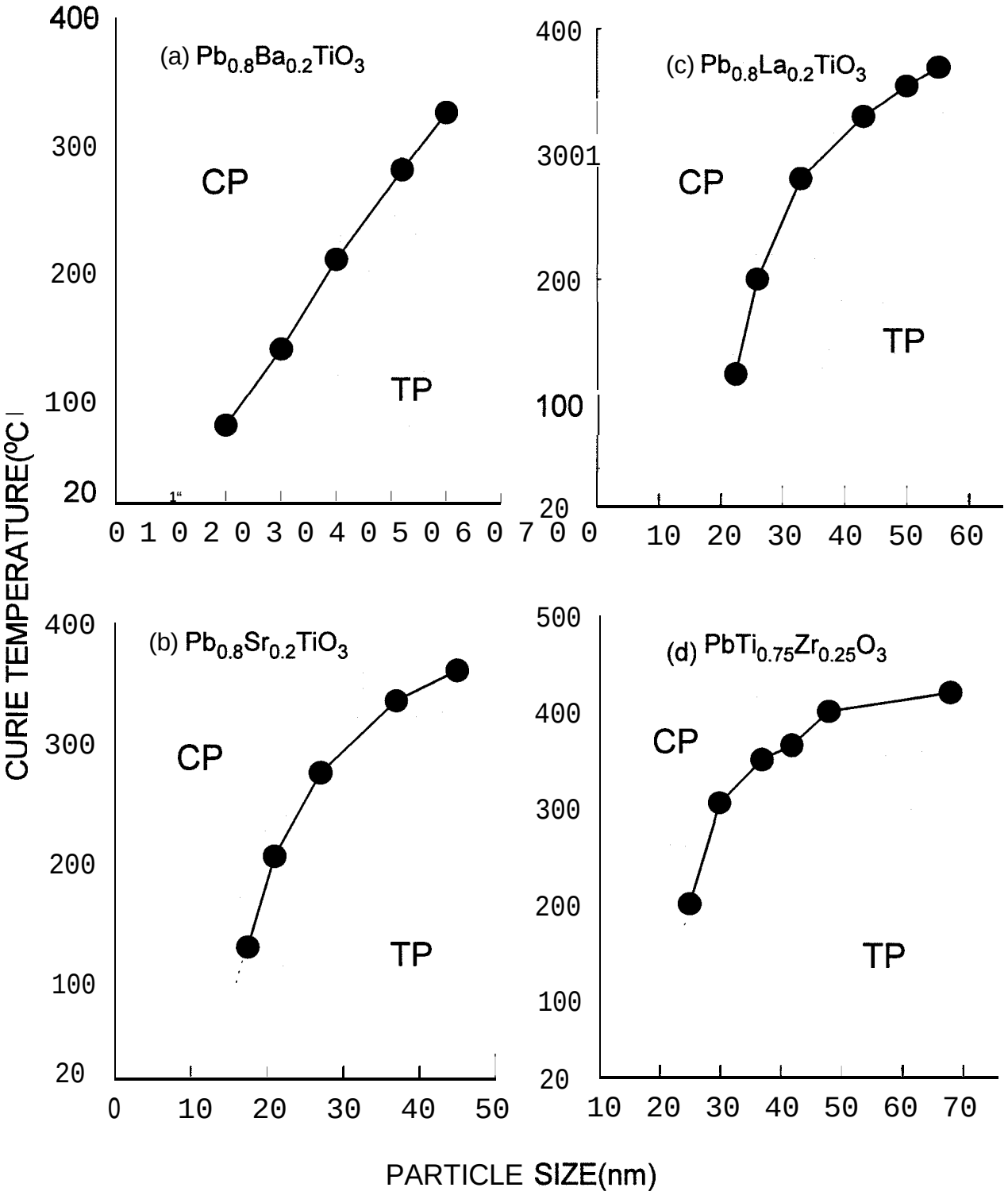

Fig. 3 The particle size dependence of Curie temperature for nanocrystalline

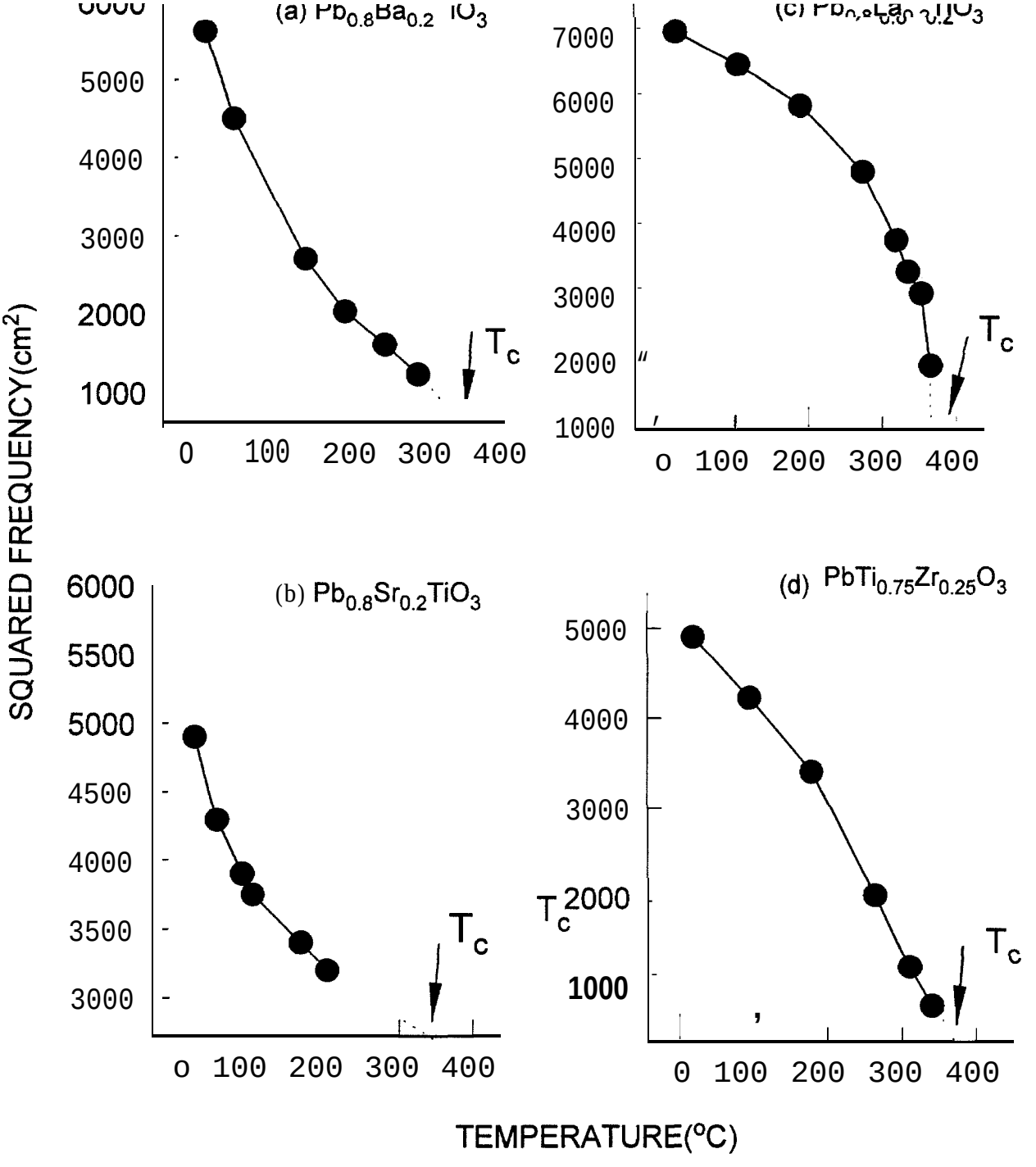

Fig. 2 The temperature dependence of the squared frequency of the soft mode