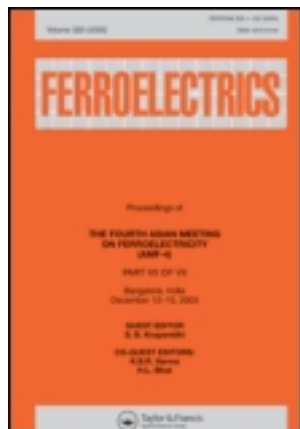


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Effects of inhomogenous strain in ferroelectric crystals near their phase transitions

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EFFECTS OF INHOMOGENOUS STRAIN IN FERROELECTRIC CRYSTALS NEAR THEIR PHASE TRANSITIONS

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Measurements of the temperature dependence of the heat capacity in LiNH_4SO_4 , $\text{Gd}_2(\text{MoO}_4)_3$, $\text{Th}_2(\text{MoO}_4)_3$ and $\text{Ni}_3\text{B}_7\text{O}_{13}\text{Br}$, near their ferroelectric phase transitions, exhibit multiple peaking. An explanation of this behavior based on strains induced during crystal growth and/or sample fabrication is offered.

INTRODUCTION

During a study of the thermal properties of ferroelectric crystals in the molybdate and boracite families, we observed anomalies in the temperature dependence of the heat capacity (C_p). These anomalies appear as "multiple peaks" and occur within a narrow temperature range in the immediate vicinity of the ferroelectric phase transition. A search of the literature revealed similar effects had only been reported by Ullman, *et al.* in pyroelectric current measurements on $\text{Gd}_2(\text{MoO}_4)_3$, and by Hoshino, *et al.* on $(\text{NH}_4)_2\text{SO}_4$ and $(\text{ND}_4)_2\text{SO}_4$.¹⁻³ They attributed the effect to thermal gradients causing non-uniform stresses across their samples which resulted from the ferroelastic nature of $\text{Gd}_2(\text{MoO}_4)_3$.² However, measurements of the temperature dependence of C_p in $\text{Gd}_2(\text{MoO}_4)_3$, near the ferroelectric phase transition did not exhibit the same multiple peaking phenomenon.⁴

The present observation of this multiple peaking in C_p measurements of a large number of different ferroelectric materials indicated the effect was worthy of further investigation. Normal ferroelectrics, such as TGS and DTGFB did not exhibit the multiple peaking effect.

EXPERIMENTAL

The heat capacity (C_p) data was recorded on a Perkin-Elmer Model DSC-2 differential scanning calorimeter‡ at scanning rates 0.3 to 10 K min⁻¹ and sensitivities in the range 0.2 to 1.0 mcal sec⁻¹. The temperature scale was calibrated using the melting point of pure indium (429.7°K). The calorimeter sensitivity was calibrated with crystalline Al_2O_3 by comparison with C_p values published by NBS and the ΔH of fusion of pure indium (6.8 cal/g).⁵ Samples were in the form of thin flat plates ranging in weight from 10 to 50 mg. These samples were not electroded, therefore the values of C_p do not correspond to constant electric field. The overall accuracy of the C_p measurements was better than 1%. Relative measurements on a single sample are accurate to 0.25%.

The boracite crystals measured were all grown from the vapor phase as described by Schmid.⁶ In addition, vapor grown samples of $\text{Ni}_3\text{B}_7\text{O}_{13}\text{Br}$, supplied by F. W. Ainger and R. Whatmore (Plessey Company) and T. Gier (DuPont Company) were also measured. Several vapor grown

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‡ Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

crystals of $\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$ were also supplied by J. Kobayashi (Waseda University). The crystals of $\text{Gd}_2(\text{MoO}_4)_3$ and $\text{Tb}_2(\text{MoO}_4)_3$ were grown by the Czochralski method as previously reported.⁷ Melt grown samples of $\text{Tb}_2(\text{MoO}_4)_3$ and $\text{GdDy}(\text{MoO}_4)_3$ were also supplied by T. Gier (DuPont). Single crystals of LiNH_4SO_4 were grown from saturated aqueous solutions (40°C) by the temperature lowering method.⁸

RESULTS AND DISCUSSION

An example of multiple peaking in the heat capacity of $\text{Ni}_3\text{B}_7\text{O}_{13}\text{Br}$, at the (43m)-mm2 phase transition is shown in Figure 1. The individual data points are reproducible with only small fluctuations (<10%) occurring in the various C_p peaks. Repeated thermal cycling of the sample through successive heat/cool runs resulted in identical thermograms. The measured heat of transition (ΔH) in multiple peaked $\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$ and $\text{Ni}_3\text{B}_7\text{O}_{13}\text{Br}$ are $1145 \pm 110 \text{ J mol}^{-1}$ and $2600 \pm 125 \text{ J mol}^{-1}$ respectively. These values are in good agreement with those measured on single peaked samples; $1145 \pm 110 \text{ J mol}^{-1}$ and $2845 \pm 150 \text{ J mol}^{-1}$. Similar behavior was also observed in single crystals of LiNH_4SO_4 , $\text{Gd}_2(\text{MoO}_4)_3$, $\text{Tb}_2(\text{MoO}_4)_3$ and $\text{GdDy}(\text{MoO}_4)_3$. The number of peaks is not significant; some

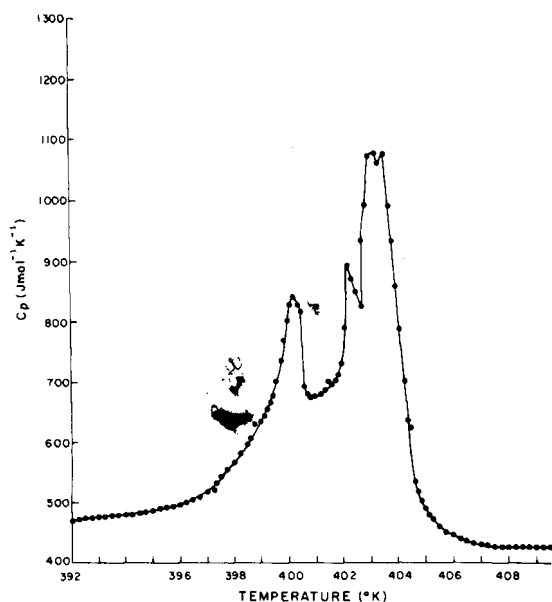


FIGURE 1 Multiple peaking in the molar heat capacity of $\text{Ni}_3\text{B}_7\text{O}_{13}\cdot\text{Br}$.

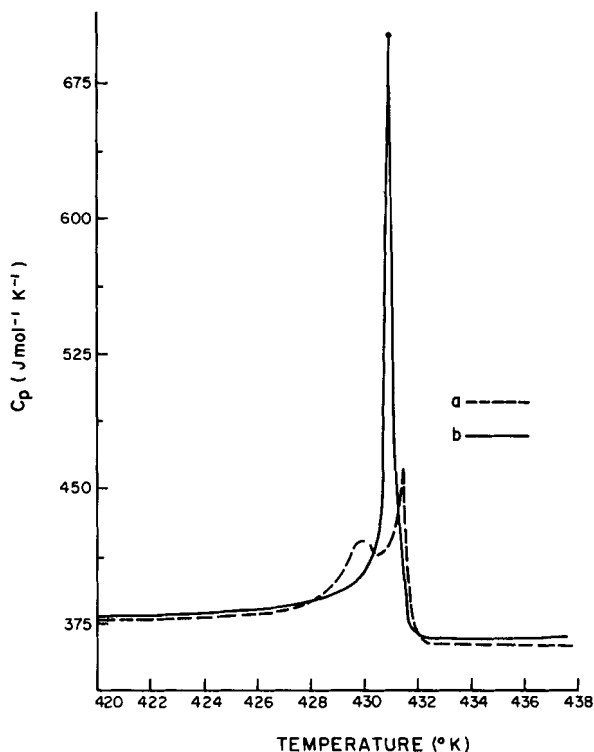


FIGURE 2 Molar heat capacity of $\text{Tb}_2(\text{MoO}_4)_3$; a) before, and b) after thermal annealing.

samples of the same compound had up to six peaks. It does appear that on a qualitative basis the greater the number of peaks the larger the internal strain in the sample. Therefore, it is clear that the anomalous peaks are not caused either by local thermal transients or partial ferroelectric domain switching, which would require compositional non-uniformities.

The source of multiple peaking was assumed to be related to internal strains generated in the materials from stresses induced during the crystal growth process. In addition, the fabrication (cutting, polishing, etc.) of samples from these crystals could also cause internal stresses. Thus, thermal annealing of the samples should remove the stresses responsible for these strains. A crystal of $\text{Tb}_2(\text{MoO}_4)_3$, which exhibited multiple peaking was wrapped in platinum foil and annealed at 960°C for 24 hours. The furnace was then cooled at a linear rate of 12°C hr^{-1} . Figure 2 illustrates the behavior of the heat capacity before and after the annealing process. The measured heat of transition ($\Delta H = 255 \pm 26 \text{ J mol}^{-1}$) was the same in both the multiple and single peaked samples, as

one would expect, if the multiple peaking was a strain-induced effect.

In a second experiment, a single crystal (001) plate of $\text{Tb}_2(\text{MoO}_4)_3$, which did not exhibit multiple peaking, was subjected to a compressive pressure of about $1 \times 10^6 \text{ N-m}^{-2}$. The pressure was applied perpendicular to the plate. This small pressure was sufficient to induce multiple peaking in the sample. In fact, repeated applications of similar pressures on the same sample resulted in significantly different thermograms. Clearly, the preparation of samples of ferroelectric crystals for measurements must be carefully performed.

The basic design of the calorimeter and the small sample size used in these measurements, make the presence of thermal gradients across the sample unlikely. Thus the multiple peaking effect is not a result of thermal gradients coupling with the ferroelastic properties of these materials. The effect is, however, a direct result of internal stresses generated in the crystals during either the crystal growth process or from subsequent fabrication of samples. The effect should only be observed in those ferroelectrics which possess significant ferroelastic coupling. In addition, the observation of multiple peaking in the measurement of other properties (i.e. dielectric) could also be attributed to internal stresses in the crystalline samples.

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REFERENCES

1. F. G. Ullman, B. N. Ganguly, and J. R. Hardy, *Ferroelectrics*, **2**, 303 (1971).
2. F. G. Ullman, K. M. Cheung, G. A. Rakes, and B. N. Ganguly, *Ferroelectrics*, **9**, 63 (1975).
3. S. Hishino, K. Vedam, Y. Okaya, and R. Pepinsky, *Phys. Rev.*, **112** (2), 405 (1958).
4. K. M. Cheung and F. G. Ullman, *Phys. Rev.*, **B10**, 4760 (1974).
5. D. C. Ginnings and G. T. Furukawa, *J. Am. Chem. Soc.*, **75**, 1397 (1953).
6. G. Schmid, *J. Phys. Chem. Solids*, **26**, 973 (1965).
7. K. Nassau, H. J. Levinstein, and G. M. Loiacono, *J. Phys. Chem. Solids*, **26**, 1805 (1965).
8. G. M. Loiacono, M. Delfino, W. A. Smith, M. I. Bell, A. Shaulov, and Y. T. Tsuo, *Ferroelectrics*, **23**, 89 (1980).

