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THERMAL DECOMPOSITION OF $\text{Nd}_3(+)$ $\text{Sr}_2(+)$ AND $\text{Pb}_2(+)$
EXCHANGED BETA' ALUMIN. (U) CALIFORNIA UNIV LOS
ANGELES DEPT OF MATERIALS SCIENCE AND ENG.

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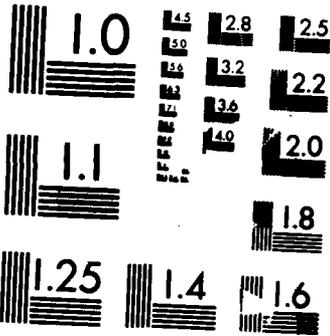
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Thermal Decomposition of Nd³⁺, Sr²⁺ and Pb²⁺ Exchanged Beta" Aluminas

by

B. + a''

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Thermal Decomposition of Nd^{3+} , Sr^{2+} and Pb^{2+}
Exchanged β'' Aluminas

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Powders of Nd^{3+} , Sr^{2+} , and Pb^{2+} β'' aluminas were prepared by ion-exchange of Na^+ β'' alumina. On heating to temperatures ranging from 850°C to 1700°C, XRD analysis indicates that Nd^{3+} and Pb^{2+} β'' aluminas start to decompose at around 1000°C. Sr^{2+} β'' alumina remains unaffected to temperatures of 1300°C. The mechanism of the decomposition process and the resultant phase transformations are different for each case.

INTRODUCTION

Sodium β and β'' alumina are non-stoichiometric compounds known for their high Na^+ ion conductivities. The structures consist of spinel like layers of closely packed Al^{3+} and O^{2-} ions interleaved by loosely packed Na^+ and O^{2-} ions; the interlayer permits fast Na^+ ion movement in two dimensions. The unit cell of β alumina consists of two spinel blocks with hexagonal structure, whereas that of β'' alumina consists of three spinel blocks with rhombohedral symmetry.

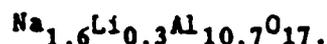
While it has long been known that a variety of monovalent cations (including protons, hydronium, and ammonium, etc.) can entirely replace Na^+ in either β or β'' alumina without affecting the basic structure and retain relatively high ionic conductivity (1) (2). Recently, this phenomenon was found to be extendable to such divalent and even trivalent cations in the β'' alumina structure (3) (4). A wide range of such β'' alumina isomorphs have now been prepared by molten salt ion exchange techniques; the resulting multivalent β'' alumina compositions possess uniquely high ionic conductivity and interesting optical properties. The divalent β'' aluminas generally exhibit conductivities of about $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 300°C . One remarkable exception, Pb^{2+} β'' alumina, has a conductivity comparable to that of Na^+ β'' alumina (3). The trivalent β'' aluminas, such as the Gd^{3+} , exhibit conductivity at 300°C of approximately $10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ (4). The rare earth ions introduced in β'' alumina may be optically active, and further, laser action was observed in single crystal platelets of Nd^{3+} ion-exchanged β'' alumina (5). Abnormally high oscillator strength, long fluorescence lifetime and lack of concentration quenching effect were found in the $\text{Na}^+/\text{Nd}^{3+}$ β'' alumina. The refractory nature and the chemically stable β'' alumina structure, combined with the unique properties described above, make the various β'' alumina compositions of interest for a variety of applications such as heavy metal sensors, new laser and phosphor host materials, etc.

Multivalent β'' aluminas, however, are metastable materials; synthesized at relatively low temperatures ($500\text{--}800^\circ\text{C}$), they are susceptible to higher temperature degradation. Since all the isomorphs have been synthesized by ion exchange, approximately one half or one third of the original number of cations populate the conduction layer of di- or tri-valent β'' alumina, making the already very open spaced layer even more defective. Although these vacancies may contribute to fast ion motion, the stability of the resulting structure is expected to be reduced by them.

An investigation of the thermal stability of the multivalent β'' aluminas is needed to assess the temperature limit for potential applications, and to comprehend the decomposition processes; here we report the preparation, thermal stability and decomposition reactions of three compositions, viz., Nd^{3+} , Pb^{2+} and Sr^{2+} β'' aluminas, chosen in the anticipation of rather different results.

EXPERIMENTAL

To prepare phase-pure, lithium stabilized sodium β'' alumina, a chemical mixing technique was employed. A reactive $\text{AlO}(\text{OH})$ boehmite* powder was blended with isopropanol, calculated amounts of aqueous solutions of NaNO_3 and LiNO_3 (Na:Li:Al ratio is about 1:1/4:5) were added into the rotating aluminum blades of a blender to achieve good homogeneity. The resultant gel-like mixture was blow-dried and subsequently vacuum dried at 120°C . The dried mixture was then very lightly milled and reacted. Single-phase sodium β'' alumina, viz., no β alumina XRD peaks and no apparent syntactic intergrowth, was produced by sintering the mixture buried in powder of the same composition, at a temperature of 1500°C in air for a few hours. The composition so obtained is:



Multivalent β'' alumina isomorphs were prepared by molten salt ion exchange processes under the conditions described previously for single crystal samples (3) (4). Table 1 indicates conditions for preparing Nd^{3+} , Pb^{2+} and Sr^{2+} β'' aluminas. Careful washing procedures are critical in order to obtain clean samples devoid of residual ion exchange chemicals. Samples thus prepared were analyzed by XRD**. The β'' structure was preserved during ion exchange processes and the sodium content was undetectable by EDS.***

Decomposition was carried out by heating the samples in air to specified temperatures and quenching from the furnace. Debye-Scherrer XRD analysis (performed at room temperature) revealed the phase transitions of Nd^{3+} , Sr^{2+} and Pb^{2+} ion exchanged β'' aluminas after high temperature firing.

RESULTS AND DISCUSSION

For Nd^{3+} β'' alumina, a comparison of the XRD patterns at different temperatures (Fig. 1a) shows that the original β'' structure remains unaffected when heated to 850°C . At 1000°C , some initial degradation is indicated, with substantial collapse of the β'' structure occurring at 1050°C . Between 1100 - 1250°C , β'' alumina phase is totally transformed into perovskite type NdAlO_3 and a δ -type alumina structure.

* Dispural, Remet Chemical Corp., Chadwicks, NY.

**Diano Corp., Woburn, MA.

*** Tracor Northern 2000

The δ -type alumina has a tetragonal structure with $a = 0.7928$ nm, $c = 1.1715$ nm. Its prototype, stabilized by MgO, NiO or Li_2O , was first reported by Lejus (6), who obtained it by quenching samples from temperatures of 1800 to 2100°C. Apparently the δ -type phase resulting from Nd^{3+} β'' alumina decomposition is metastable; it then reacts at higher temperatures with NdAlO_3 in a second stage wherein α -alumina and a magnetoplumbite (MP) type phase begin to crystallize at $\sim 1350^\circ\text{C}$, the δ -type alumina phase disappears at $\sim 1450^\circ\text{C}$ (Fig. 1b).

The MP structure is superficially similar to that of β alumina; its unit cell consists of two spinel blocks, which are separated by a mirror plane layer containing nearly close-packed O^{2-} and Al^{3+} ions, with large divalent or trivalent cations stuffing the layer. It has been demonstrated that the c/a ratio can be used as a simple criterion to distinguish the closely related β type and MP type of structures (7). The MP type phase resulting from the decomposition of Nd^{3+} β'' alumina has $a = 0.5561$ nm, $c = 2.1910$ nm, and $c/a = 3.940$. These values are similar to those for a Li-Nd magnetoplumbite phase reported by Liebertz (8), who claimed to prepare $\text{NdLi}_{0.5}\text{Al}_{11.5}\text{O}_{19}$ by solid state reaction; although we have doubts about this stoichiometry (9). There are no superlattice lines detected in the XRD pattern; the MP phase appearing at the relatively low temperatures is apparently stabilized by the lithium, since neither MP nor β alumina type neodymium aluminate can be made by solid state reaction at temperatures below 1500°C (10). We assume the formula of the MP composition to be $\sim \text{Nd}_{0.75}\text{Li}_{0.5}\text{Al}_{11.75}\text{O}_{19}$.

The Sr^{2+} β'' alumina is more stable than the Nd^{3+} isomorph. The β'' structure remains until 1300°C . By 1400°C , phase transformation starts, the XRD pattern at 1500°C shows the β'' phase coexists with the decomposition product, which was identified as a β type phase (Fig. 2a and b), similar to that reported by Versteegen and Stevels (7), who prepared a compound with a composition $\text{SrMgAl}_{11}\text{O}_{18.5}$, in which Mg^{2+} substitutes for Al^{3+} . The high c/a ratio ($= 3.980$) suggests the structure is more β like than MP type. By using high angle, accurate XRD, the β type phase resulting from the decomposition of Sr^{2+} β'' alumina was found to have $a = 0.5601$ nm, $c = 2.2364$ nm, $c/a = 3.993$, and presumably contains the lithium replacing the magnesium of the compound mentioned above.

Further heating the partially decomposed Sr^{2+} β alumina to about 1600°C , left no β'' phase in the XRD pattern; but splittings of high angle peaks of the Sr β type phase was readily observed (Fig. 3). The splitting results from the progressive transformation of β type structure to MP type structure. When the sample was heated to 1700°C , the MP type phase predominates. This Sr

magnetoplumbite was analyzed to have $a = 0.5568$ nm, $c = 2.2022$ nm, and $c/a = 3.955$. The MP phase is not formed simply by gradual diffusion of Al^{3+} ions into the interlayers from the spinel blocks, since no transitional broadening of the β phase peaks is observed. The sharpness of the split peaks in Fig. 3 indicates that a reconstructive recrystallization process is responsible for the formation of the MP phase; this perhaps is a surprising result.

The decomposition processes of Nd^{3+} and Sr^{2+} β'' aluminas demonstrate the phase relationship among this aluminate family at high temperatures, the "2-block" β or MP structure is more stable than the "3-block" β'' structure, and the MP phase has the greater stability when lithium is present. The conversion of β'' to either β or MP structure, however, does not occur at temperatures below about $1000^\circ C$. In the case of decomposition of Nd^{3+} β'' alumina, it is easiest to go via an intermediate δ -type alumina phase before the formation of magnetoplumbite. Perhaps at $1000^\circ C$ either diffusion is insufficiently fast or nucleation barrier too high to allow the immediate reconstructive rearrangement of 3-block type to 2-block type. On the other hand it is not obvious that the δ form is the result of any kind of topochemical collapsed structure. Sr^{2+} β alumina crystallizes out directly from the β'' matrix at temperatures around $1400^\circ C$. Diffusional mechanisms now at $1400^\circ C$ seem to be sufficient to allow this direct conversion.

Pb^{2+} exchanged β'' alumina decomposes in a different, more complex way, than the other two isomorphs. Pb^{2+} β'' alumina begins to change at around $1000^\circ C$, forming an unknown phase which is represented by the cross-hatched peaks shown in the XRD pattern in Fig. 4. Minor rearrangement of the spinel blocks as PbO evolved (as by the spinel blocks collapsing upon each other) is thought in some not obvious fashion to result in formation this phase. Preliminary TGA* experiments indicated a very slow rate of weight loss when isothermally heating Pb^{2+} β'' alumina at $1000^\circ C$. EDS analysis detected no Pb in the sample when it was heated above $1400^\circ C$, at which the unidentified phase further decomposed into α -alumina and another unknown phase (Fig. 5). The decomposition mechanism of Pb^{2+} β'' alumina is thought to be somewhat similar but not identical to that of NH_4^+/H_3O^+ β'' alumina reported by Thomas et al (11), in which the deamination of NH_4^+/H_3O^+ β'' alumina on heating above $200^\circ C$ collapsed the β'' structure. They also observed loss of alternate conduction layers due to NH_3 evolution, leaving broad defect spinel blocks corresponding to two original spinel blocks without the interlayer. Attempts to index the phase on the basis of rational types of unit cell that might be produced by simple stacking of defect spinel blocks did not succeed, however, ongoing

*DuPont 1090 Model 951

investigation is still trying to elucidate this point.

CONCLUSION

The decomposition nature of various multivalent ion exchanged β'' aluminas is determined by the chemistry in the conduction layer and the stability of various products as a function of temperature. Replacing Na^+ with other divalent or trivalent cations indeed substantially reduces the thermal stability of the structure. Although divalent β'' alumina appears to be more stable than trivalent β'' alumina, as in the case of Sr^{2+} β'' alumina versus Nd^{3+} β'' , it would very much depend upon the nature of the species occupying the conduction layer. High volatility of PbO , for example, degrades the stability of the structure at high temperatures as compared to Sr^{2+} β'' alumina.

Planes of Pb^{2+} β'' alumina begin to collapse at $\sim 1000^\circ\text{C}$ into a minor Pb containing metastable phase, which further decomposed into $\alpha\text{-Al}_2\text{O}_3$ with volatilization of Pb . At these low temperatures, where diffusion is slow, rearrangement of planes is more likely to form metastable phases.

Nd^{3+} β'' alumina decomposes at $\sim 1000^\circ\text{C}$ into high stability NdAlO_3 and metastable δ -type Al_2O_3 . At temperatures above 1300°C , $\alpha\text{-Al}_2\text{O}_3$ and Li stabilized Nd -magnetoplumbite phase crystallize at expense of δ -type Al_2O_3 and NdAlO_3 by obviously diffusional mechanisms.

Sr^{2+} β'' alumina remains stable until $\sim 1400^\circ\text{C}$. Phase transformation of β'' to Li stabilized β structure was observed. At even higher temperatures, a conversion of β phase to magnetoplumbite phase ensues apparently by a recrystallization mechanism. Diffusional mechanisms are the main mode of transformation and small amount of liquid eutectics may be present.

A general trend for all decompositions of metastable substituted β'' aluminas would therefore seem to be that when occurring at lower temperatures (e.g., $\sim 800\text{--}1100^\circ\text{C}$) we might expect changes that partially or completely are by rearrangement mechanisms, e.g., collapse of spinel blocks leading to metastable intermediates. At higher temperatures, progressively increasing diffusion and surmountable nucleation barriers will allow the formation of new stable intermediates or end products. The mode of transformation then will depend on two main features: (1) The temperature of decomposition that must coincide with the loss of an element (e.g., Pb) and (2) The availability of stable intermediates or end products (e.g., NdAlO_3) which can more easily nucleate and grow and which in turn depends on the crystal chemistry of the

doping element.

ACKNOWLEDGEMENTS

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Presented at the 87th Annual Meeting and Exposition, The American Ceramic Society, Cincinnati, Ohio, May 7, 1985 (Electronics Division, Paper No. 77-E-85).

TABLE 1: Ion Exchange Conditions for Preparation of Multivalent Beta'' Aluminas

ION	MELT(mole%)	TEMP(°C)	ATM	Time(hr)
Nd ³⁺	100NdCl ₃	800	N ₂ +Cl ₂	0.5 #
Pb ²⁺	100PbCl ₂	550	N ₂	20
Sr ²⁺	47Sr(NO ₃) ₂ * + 53SrCl ₂	550	N ₂	20

Nd³⁺ exchange time is constrained by severity of NdCl₃ melt at high temperatures

*mixed with nitrate to lower melting temperature

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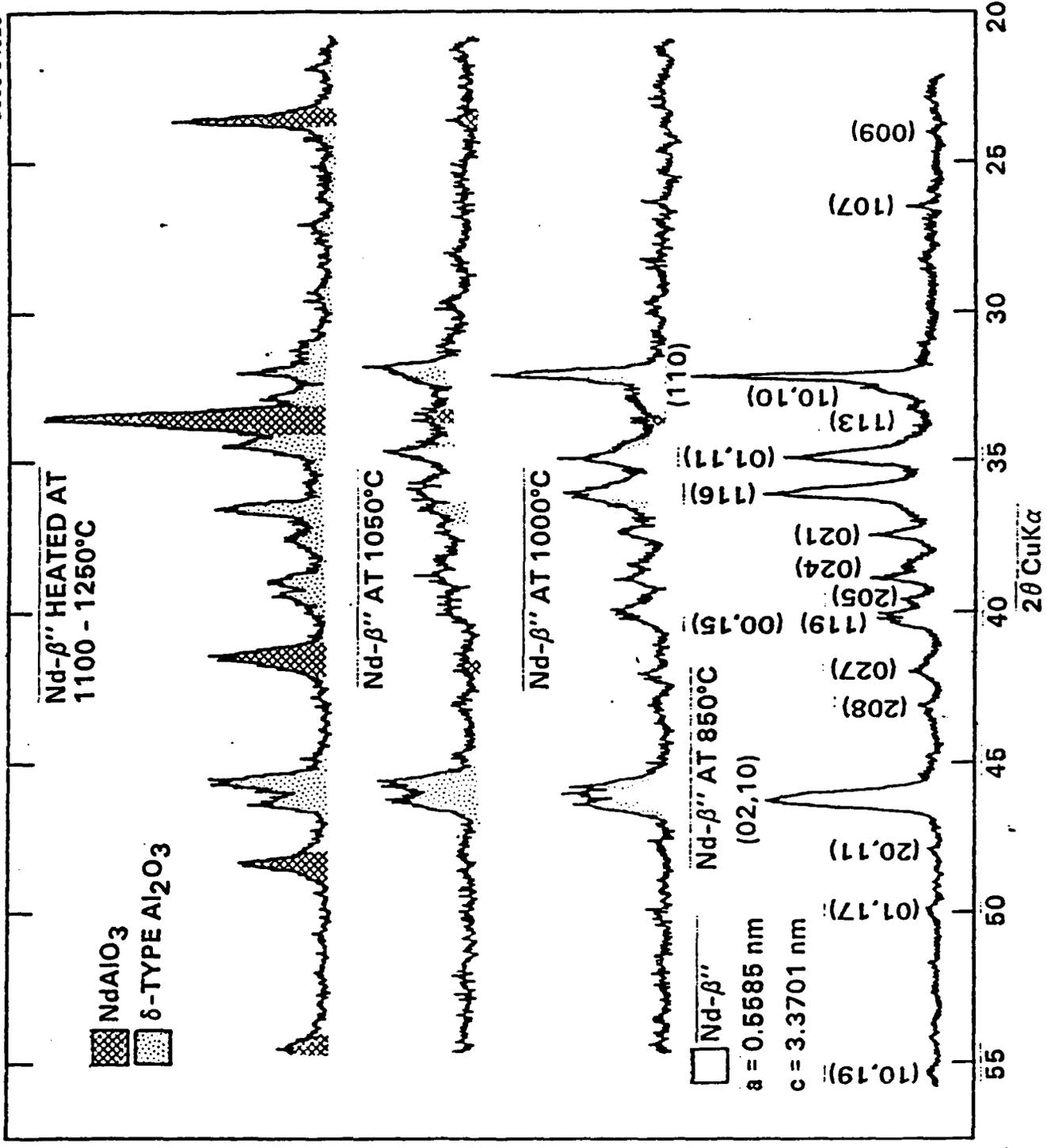
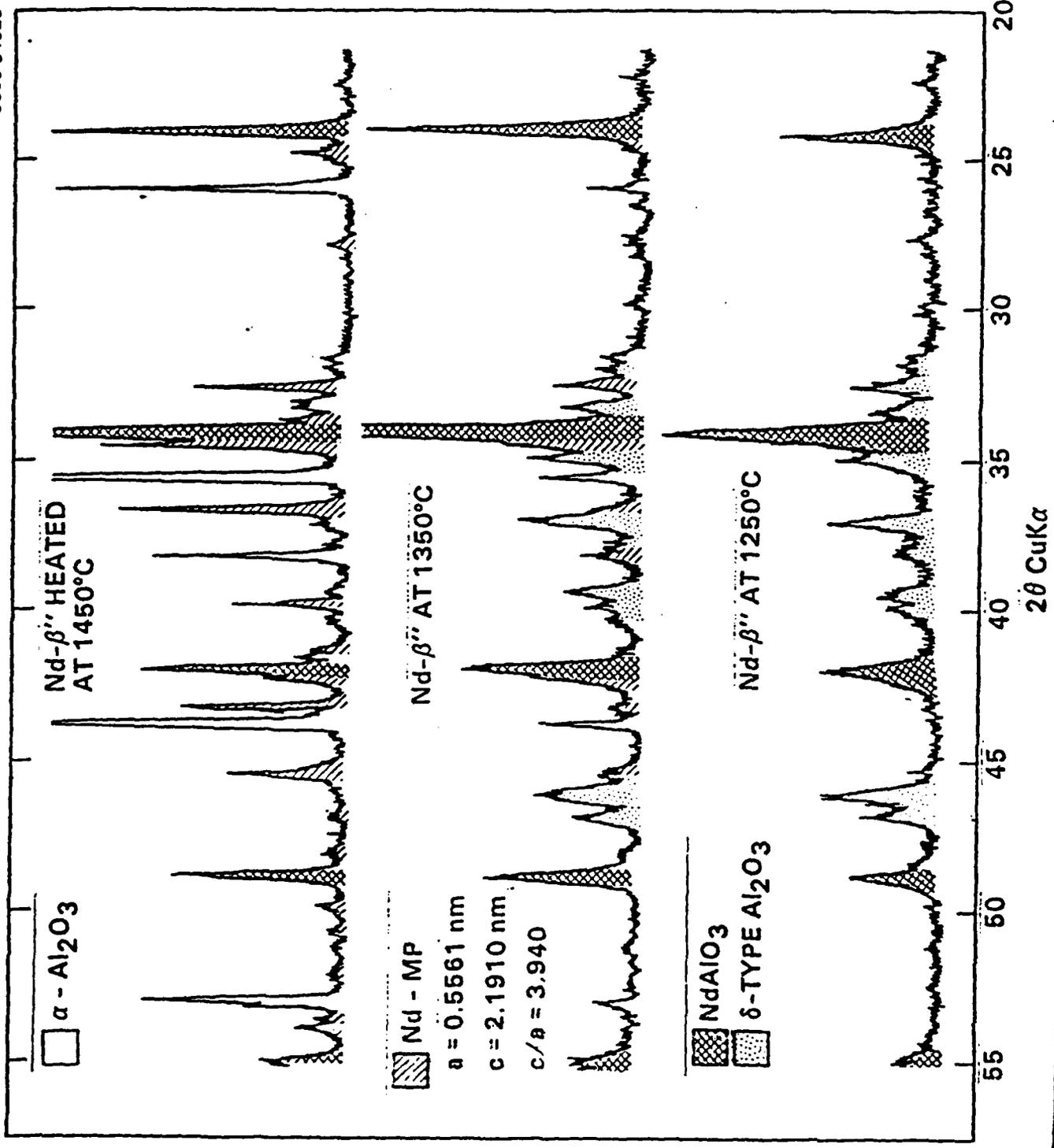


Fig. 1 a

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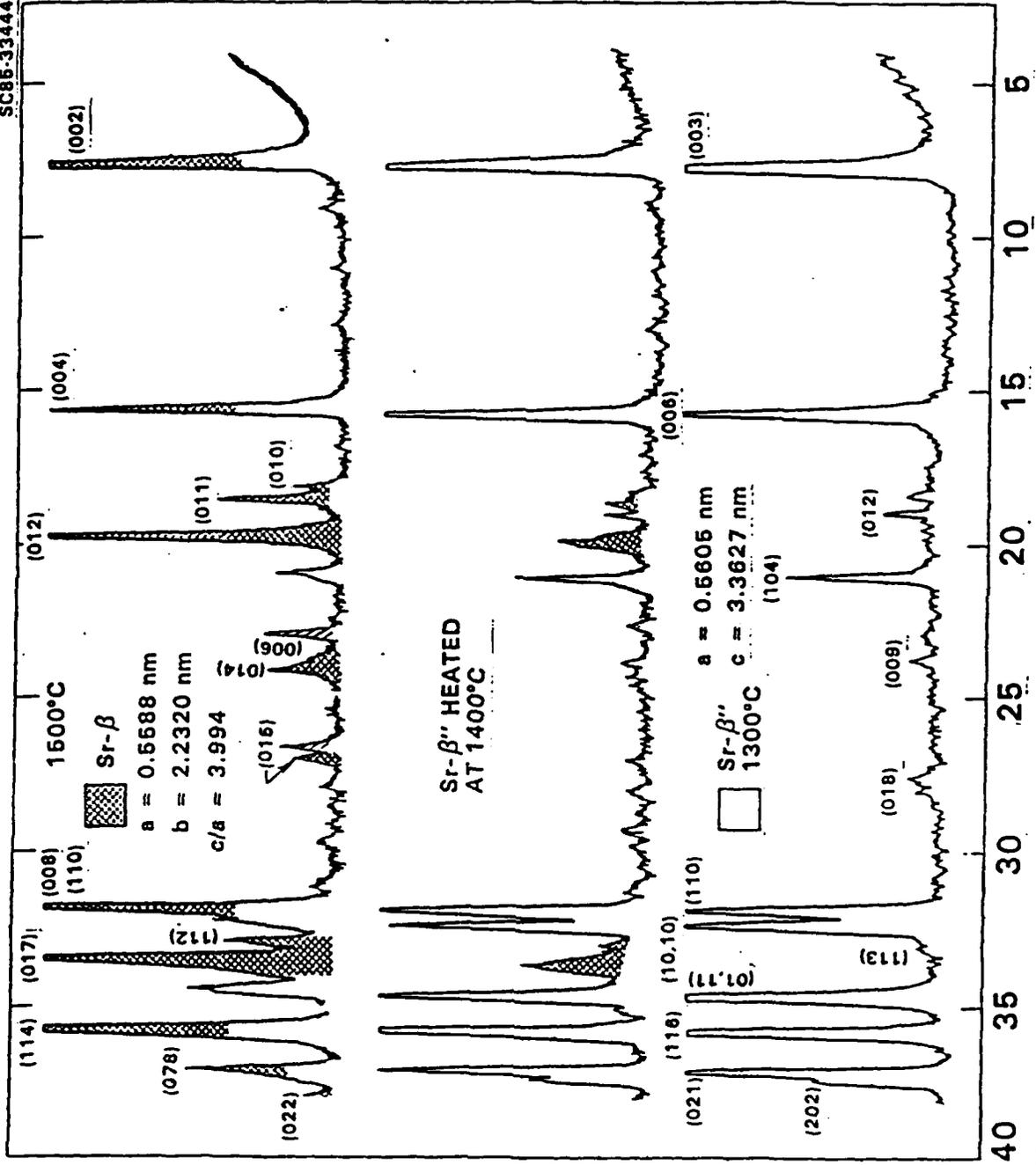


Fig. 2a

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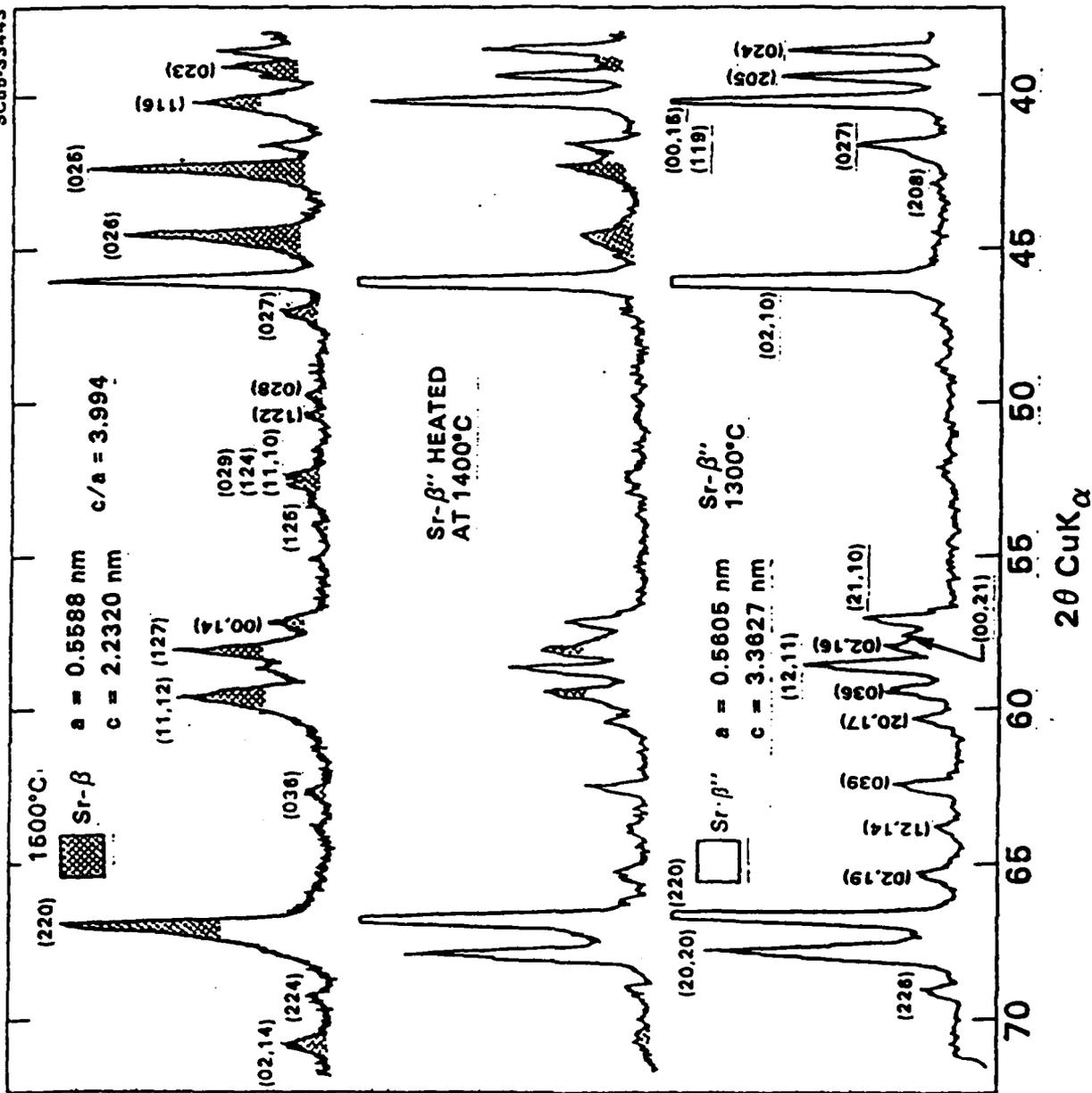


Fig. 2b

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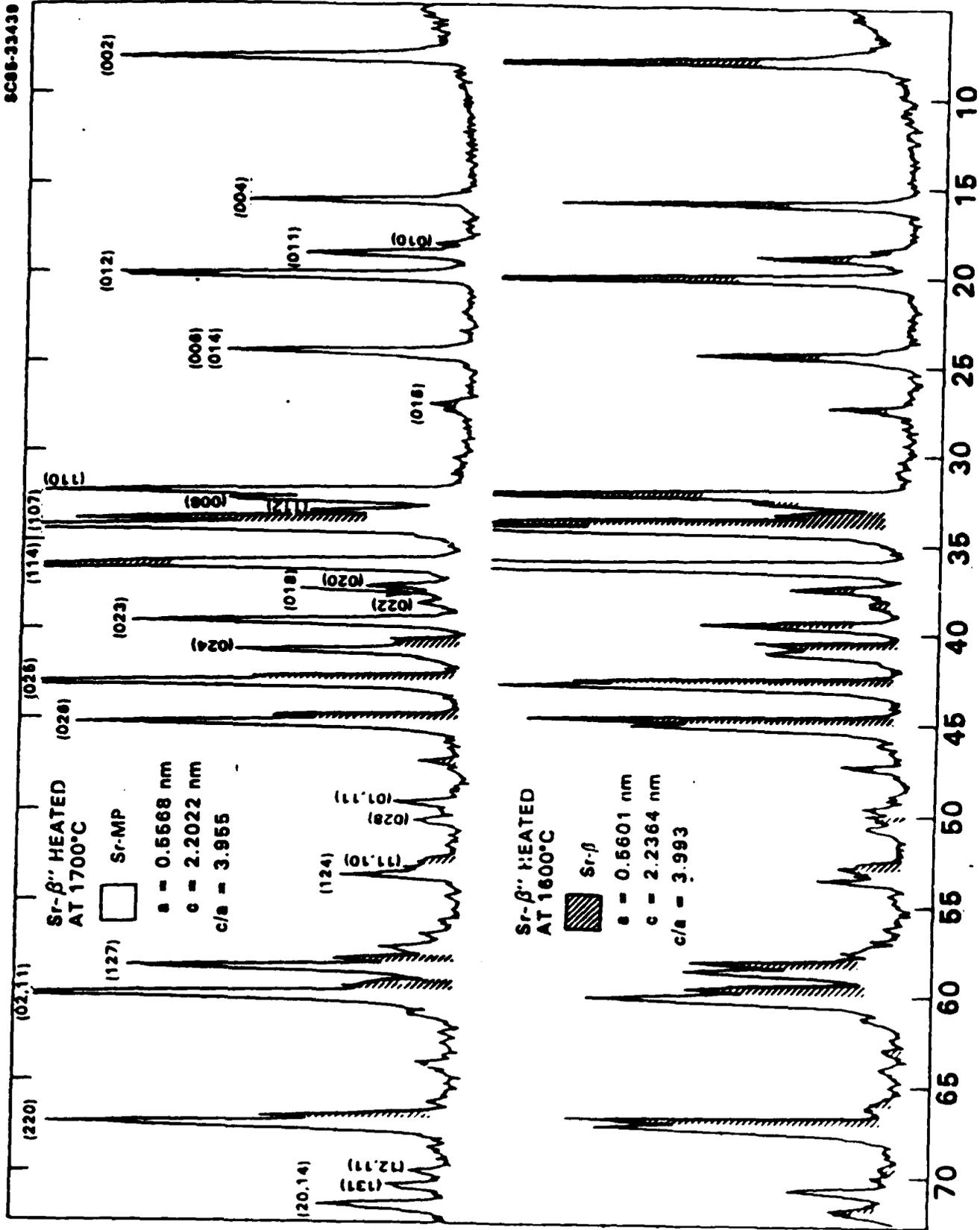


Fig 3

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Pb- β'' HEATED
AT 1000-1200°C

UNKNOWN I

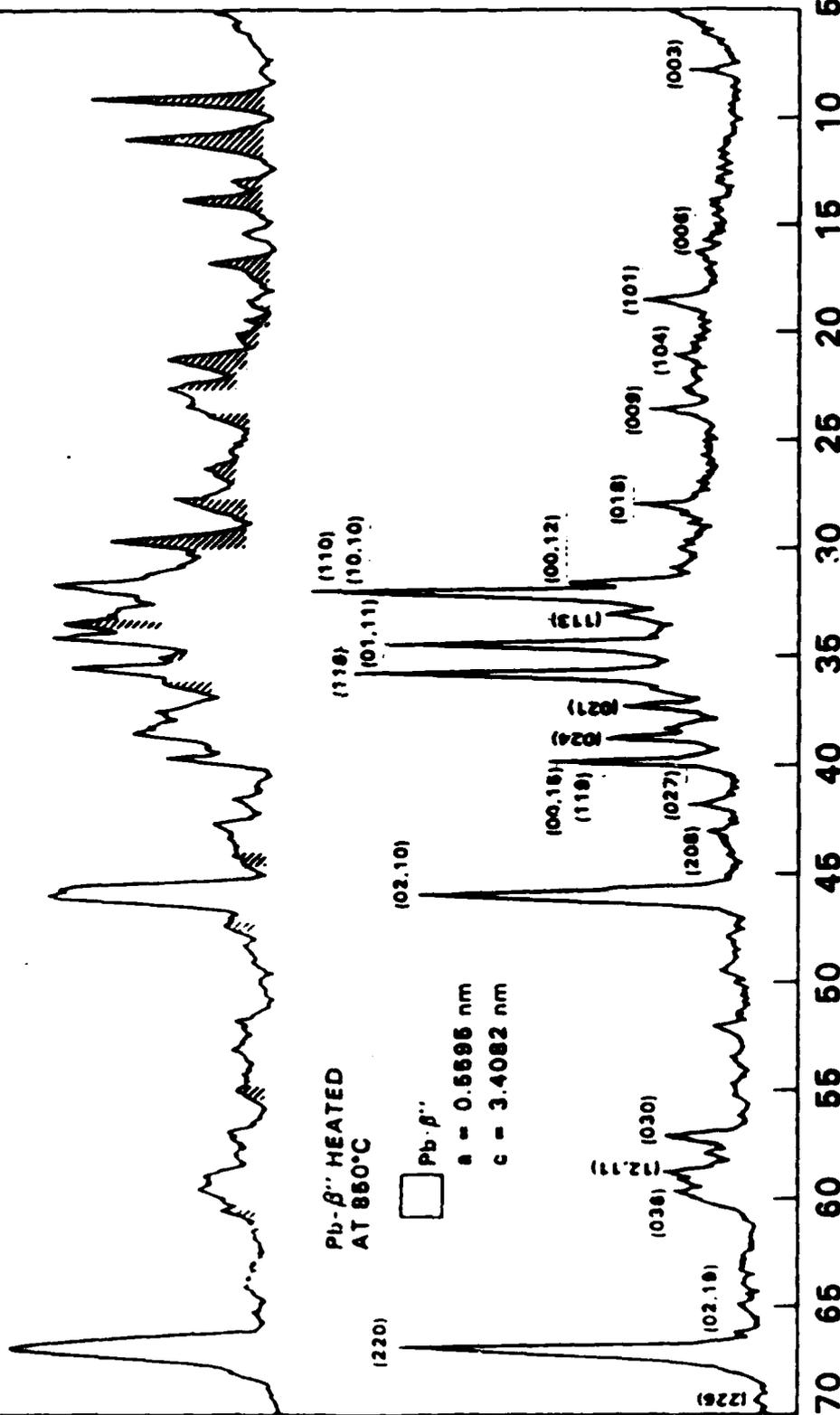


Fig 4

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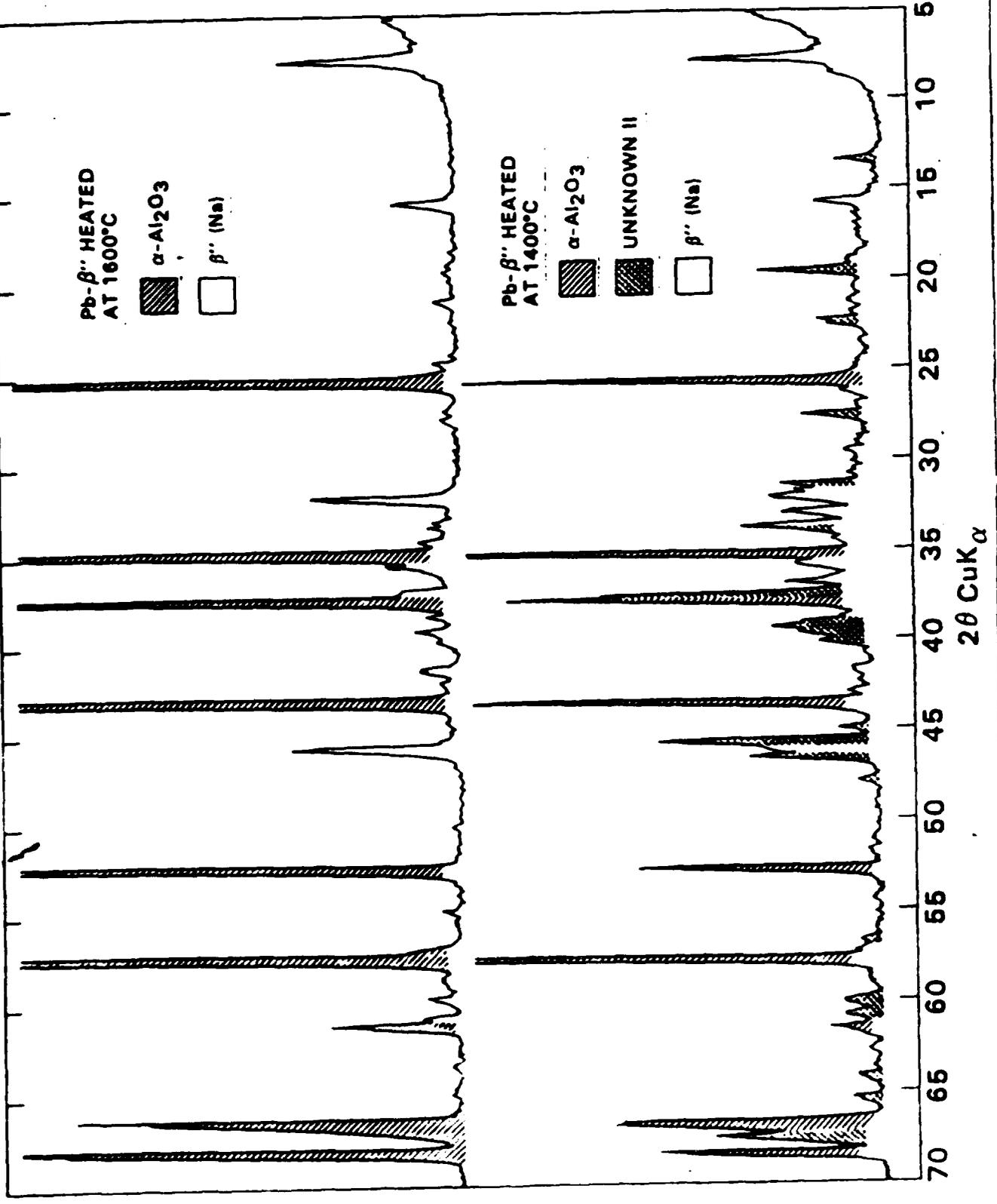


Fig 5

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Dtic